Since January 2020 Elsevier has created a COVID-19 resource centre with free information in English and Mandarin on the novel coronavirus COVID-19. The COVID-19 resource centre is hosted on Elsevier Connect, the company's public news and information website.

Elsevier hereby grants permission to make all its COVID-19-related research that is available on the COVID-19 resource centre - including this research content - immediately available in PubMed Central and other publicly funded repositories, such as the WHO COVID database with rights for unrestricted research re-use and analyses in any form or by any means with acknowledgement of the original source. These permissions are granted for free by Elsevier for as long as the COVID-19 resource centre remains active.
Simultaneous degradation of glucocorticoids and sterilization using bubbling corona discharge plasma based systems: A promising terminal water treatment facility for hospital wastewater

Xiaoting Gao\textsuperscript{a}, Keliang Huang\textsuperscript{a}, Ai Zhang\textsuperscript{a,\ast}, Cihao Wang\textsuperscript{a}, Zhuyu Sun\textsuperscript{a}, Yanan Liu\textsuperscript{a,b,\ast}

\textsuperscript{a} College of Environmental Science and Engineering, Donghua University, 2999 North Renmin Road, Shanghai 201620, China
\textsuperscript{b} Shanghai Institute of Pollution Control and Ecological Security, Shanghai 200092, China

ARTICLE INFO

Keywords:
Glucocorticoids (GCs)
Advanced oxidation processes (AOPs)
Sterilization
Non-thermal plasma (NTP)
Activated-carbon fibre (ACF)

ABSTRACT

Glucocorticoids (GCs) have drawn great concern due to their widespread contamination in the environment and application in treating patients with COVID-19. Due to the lack of data about GC removal using advanced treatment processes, a novel Paralleling and bubbling corona discharge reactor (PBCD) combined with iron-loaded activated-carbon fibre (Fe-ACF) was addressed in this study to degrade GCs represented by Hydrocortisone (HC) and Betamethasone (BT). The results showed that the PBBCD-based system can degrade GCs effectively and can achieve effective sterilization. The removal rates of GCs were ranked as PBCD/Fe-ACF > PBCD/ACF > PBBCD. The concentration of \textit{E. coli} was reduced from 10\textsuperscript{9} to 10\textsuperscript{2} CFU/mL after 60 min of PBBCD-based system treatment. The abundance of bacteria in actual Hospital wastewater (HWW) was significantly reduced. Plasma changed the physical and chemical properties of ACF and Fe-ACF by etching axial grooves and enhancing stretching vibrations of surface functional groups, thus promoting adsorption and catalytic degradation. For GC degradation, the functional reactive species were identified as \textit{OH}, \textit{O}_2\textit{O}, and \textit{O}_2\textit{O} radicals. Possible degradation pathways for HC and BT were proposed, which mainly included defluorination, keto acid decarboxylation, demethylation, intramolecular cyclization, cleavage and ester hydrolysis, indicating a reduction in GC toxicity.

Since GCs are widely used in patients with COVID-19 and their wastewater needs to be sterilized simultaneously, the intensive and electrically driven PBBCD-based system is promising in GC pollution control and sterilization in terminal water treatment facilities.

1. Introduction

Glucocorticoids (GCs) are a class of steroid hormones that influence the immune system response, stress adaption and energy metabolism in vertebrate animals. Due to their important physiological functions, various natural and synthetic GCs (>30 kinds) are highly prescribed drugs used for various diseases [1]. The consumption of total prescribed GCs accounts for 64\% of the total clinical use of steroids [2]. The latest research shows that GCs are ubiquitous in environmental water bodies and may have reached a level that negatively affects humans and aquatic organisms [3]. A study published in Nature reported that the concentration of GCs (dexamethasone) in a river in France reached 10 μg/L [4]. Taking into account the increase in GC usage and emission, there is an urgent need to control GC pollution [5].

Hospital wastewater (HWW) is one of the sources of environmental pollution caused by GCs [6,7]. It can be seen from Table S1 of the supplementary information (SI), various GCs have been found in the HWW in many countries, with total concentrations ranging from 1 to 2000 ng/L [6–8]. Moreover, since GCs were widely used during the outbreaks of severe acute respiratory syndrome (SARS)-CoV [9] and Middle East respiratory syndrome (MERS)-CoV [10] and are now being used in patients with COVID-19 [11], HWW could be loaded with increasing concentrations of GCs. As traditional treatment processes involved in wastewater treatment plants (WWTPs) are not fully effective in eliminating GCs [12], effective treatment technologies are needed to remove GCs in HWW. In addition, HWW contains a large number of pathogenic microorganisms, parasites and various viruses [13]. Without proper treatment, it will pollute water sources and threaten public safety [14].

The currently available HWW treatment methods mainly include
medical microbiological methods, chemical and biochemical methods, membrane bioreactor and nanofiltration technologies, and their combinations [15]. However, most methods are inefficient, unstable, chemically consuming, or require dirty filters to be treated after use [15]. The commonly used disinfection techniques for HWW are ozone, ultraviolet radiation and chlorination [13,14]. The current main disadvantages of these technologies are the generation of disinfection by-products and the regeneration of pathogens [16]. In this study, an HWW treatment system using Non-thermal plasma (NTP) at atmospheric pressure was developed to solve the above disadvantages. NTP treatment uses a high voltage to ionize gases between two electrodes, generating a series of free radicals (•OH, HO2•, •O2, and O3), UV irradiation, ultrasonic waves, heat, high-energy electrons (e’), and other active species (O2 and H2O2), which can oxidize and reduce contaminants [17]. NTP treatment only uses electricity without any chemicals and can operate automatically and compactly; thus, it is environmentally friendly [18]. Major types of NTP reactors include corona discharge (CD), dielectric barrier discharge (DBD), arc discharge (AC) and contact glow discharge electrolysis (CGDE) [18]. Our previous study reported that GCs could be efficiently degraded by DBD [19]. However, energy consumption and mass transfer efficiency at the gas-liquid interface are the main factors limiting its expansion [19,20].

Gas-phase CD is recognized as the most energy-efficient plasma type in water treatment due to the excitation of high-energy electrons reduces the heat loss [21]. To improve energy efficiency, parallel CD generators were used in this study to generate continuous pressurized plasma-activated gas, and the activated gas was seamlessly delivered to a bubbling reactor to treat the wastewater. Activated-carbon fibres (ACFs) are widely used in NTP systems to purify wastewater because of their good adsorption performance and large specific surface area [22-24]. To improve the mass transfer efficiency and prolong the contact time of activated gas in the bubbling reactor in this study, ACFs were used as packing to strengthen the GC removal process. Moreover, as good catalyst carriers, several researchers have suggested placing modified ACFs into DBD plasma systems to further improve contaminant removal efficiency [23]. Therefore, this work hypothesizes that CD coupled with ACFs or iron modified ACFs can degrade GCs effectively by the generated activated gas in CD and ACF-based catalysis in the bubbling reactor. To our knowledge, there have been few studies regarding the removal of GCs by CD treatment or ACF adsorption [1,18,23]. The performances of CD treatment and CD combination with ACFs or modified ACFs in GC removal have not been sufficiently examined, nor have related mechanisms been elucidated.

Based on this hypothesis, the performances and mechanisms of a novel parallel and bubbling corona discharge reactor (PBCD) and PBCD combined with ACF or iron-modified ACF (Fe-ACF) in GC removal and sterilization were evaluated in this work. Among GCs, Hydrocortisone (HC) and Betamethasone (BT) deserve particular attention and were chosen as the target GCs because they have widespread applications and high detection frequencies [2]. The physical and chemical properties of HC and BT are shown in Table 1. The synergistic mechanisms of the PBCD and ACF or Fe-ACF were explored by identifying functional reactive radicals and analysing changes in ACF and Fe-ACF during discharge by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and the Brunauer-Emmett-Teller (BET) method. The degradation pathways of GCs were proposed by revealing new intermediates through high-resolution quadrupole time-of-flight (QTOF) mass spectrometer analysis. The effects of discharge power, ACF dosage, and iron-loading ratio on the GC removal rate and energy yield were evaluated.

2. Materials and methods

2.1. Materials

HC (purity > 99%) and BT (purity > 99%) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). The stock standard solutions of HC and BT were prepared in acetone and stored at 4 °C. Acetone (99%) and acetonitrile (99%) were purchased from Shanghai Loran Chemical Reagent Co., Ltd. (Shanghai, China). All other reagents, including sulfuric acid (H2SO4), sodium hydroxide (NaOH), p-benzoquinone (C6H4O2, BQ, 99%), tert-butanol ((CH3)2OH, TBA, 99%), triethylendiamine (N(CH2CH2)2N, DABCO, 99%), terephthalic acid (CaH2O4, PTA, 99%), and 5,5-dimethyl-1-pyrroline N-oxide (DMPO), were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

All solutions used in the experiment were prepared with an actual HWW configuration with a 1.2 mm filter membrane. HWW was collected from a representative hospital in Shanghai and sampled directly from the sewer collection system of the hospital. The characteristics of the actual HWW are shown in Table S2 in the SI. The ACF used in this study was an STF1300 activated-carbon fibre manufactured by Sutong Carbon Fibre Co., Ltd. (Jiangsu, China). The characteristics of the ACF are summarized in Table S3.

2.2. Experimental apparatus

Fig. 1 exhibited the experimental setup. The system contained a
high-voltage power supply (Dalian University of Technology, China), a corona discharge bubbling reactor, a digital oscilloscope (TDS 2012B, Tektronix, Inc., China), a gas flowmeter (LZB-3WBF, Changzhou Kede Thermal Instrument Co., Ltd., China) and an air pump (AP-9925, Tianjin Auto Sains Instrument Co., Ltd., China). The power supply enabled voltage ranging from 0 to 12 kV and a frequency of 7.9 kHz. The voltage and current waveforms were recorded by oscilloscopy through a high voltage probe (Tektronix TPP0101, passive detection probe with 12 pF, 10 MΩ) and a current probe ((Tektronix P6021A). The corona discharge bubbling reactor was composed of 37 parallel microcorona-discharge-plasma spray units arranged in a regular hexagon. These units were fixed to the bottom of the quartz water tank through a perforated polytetrafluoroethylene insulation plate (62 mm in inner diameter, 67 mm in outer diameter and 120 mm in height). Each jet tube had an inner diameter of 0.7 mm and an outer diameter of 1 mm, and all were made of quartz. The quartz tube used a coaxial tungsten electrode (0.3 mm in diameter) as a high-voltage electrode, and the solution in the reactor was ground level. The air pump was connected to the reactor through a rubber tube, and a gas flow meter was used to control the air flow to the quartz tube.

2.3. Experimental procedures

2.3.1. Performance of the PBCD-based system on GC removal and sterilization

The effects of discharge power, ACF dosage, and iron-loading ratio on GC removal and energy efficiency were evaluated during PBCD-based system treatments. The air pump was turned on, and the gas flow rate was adjusted to 4 L/min. One hundred millilitres of HWW (initial pH = 7.67) contaminated by GCs at an initial concentration of 50 mg/L (considering the determination of degradation intermediates) was injected into the reactor. The presence of acetone does not affect the degradation of GC, and the relevant results were recorded in Fig. S1. ACF or Fe-ACF at the desired dosage was added to the reactor. The plasma power supply was turned on to start the reaction. Samples were withdrawn at 0, 20, and 60 min. The GC intermediates before analysis.

E. coli (CGMCC 1.1512) cultured in Luria-Bertani medium was used as a model microorganism to evaluate the bactericidal effects of the PBCD-based system. The density was determined by OD600 and the heterotrophic plate-counting method [25]. Two hundred millilitres of E. coli solution (10⁹ CFU/mL) was sterilized under the corresponding conditions for GC removal. To analyse the microbial community structure in actual HWW, 500 mL of HWW was treated with the PBCD/Fe-ACF system at 34.8 W and then enriched with a 0.2 μm membrane, followed by DNA extraction and ultragenome sequencing (Shanghai Majorbio Biopharmaceutical Technology Co., Ltd., China). All experiments were performed at an ambient temperature of 25 °C and repeated at least three times.

2.3.2. Preparation and characterization of ACF and Fe-ACF

The pretreatment methods of ACF are shown in Text S1 in the SI. The preparation process of modified ACF is shown in Fig. S2. The surface morphologies of ACF or Fe-ACF before and after PBCD-based treatments were studied using SEM (Gemini ultra plus, Zeiss, Oberkochen, Germany). Their surface functional groups were identified by FTIR (Nicolet Nexus 470, Thermo Scientific, Waltham, MA, USA) with a mass ratio (KBr: ACF or Fe-ACF) of 500:1 in the range of 500–4000 cm⁻¹. Their surface areas and micropore volumes were calculated by BET (Micromeritics, model ASAP 2000). ACF and Fe-ACF before discharge were soaked in the reactor filled with pure water for 60 min, and then dried together with ACF and Fe-ACF after discharge to measure SEM, BET and FTIR.

2.3.3. Characterization of reactive species

Free radicals generated during PBCD/Fe-ACF treatment were determined by optical emission spectroscopy (OES) using an AvaSpec-2048TEC spectrometer (Avantes, Netherlands) [26]. The detection of reactive species was achieved by electron paramagnetic resonance (EPR) spectroscopy (EMXnano231, Bruker, Germany) using DMPO as a spin trap agent. To explore the contribution rate of free radicals to GC degradation, BQ, TBA, and DABCO were added as inhibitors of •O₂⁻, •OH, and •O₂ radicals, respectively [27,28].

2.3.4. Identification of degradation intermediates

Identification of GC intermediates was achieved during PBCD/Fe-ACF treatment using an Agilent 1290 ultra-high-performance liquid chromatography (UHPLC, Dionex UltiMate 3000, USA) coupled with a QTOF mass spectrometer (Agilent 6540 QTOF, USA). The mass spectrometer scan was performed in negative ion mode during analysis. Samples were withdrawn at 0, 20, and 60 min. The GC intermediates were screened based on the difference in concentration from 0 min. Detailed information is displayed in Text S2 in the SI.

2.4. Analytical methods

2.4.1. GC analysis

HC and BT were analysed using an UHPLC (Dionex UltiMate 3000, USA) equipped with a C18 column (4.6 mm × 250 mm, 5 μm, Agilent, USA) and a UV detector. The trace concentration of GC is extracted by solid phase extraction (SPE). Detailed information is displayed in Text S3 in the SI.

2.4.2. Analysis of discharge power and energy yield

Discharge parameters, such as discharge voltage, current, and frequency, can be directly measured by a digital oscilloscope (I-V waveform was shown in Fig. S3), and discharge power can be calculated by the Lissajous figure, as shown in Eq. (1) [29]:

\[ P = \frac{V^2}{R} \]

Fig. 1. Scheme of the experimental set-up.
area of the active species with contaminants [33,34]. The iron introduction to the PBCD/ACF system can be established. The addition of ACF can provide the 

\[
P = \frac{1}{T} \int_0^T V_p \times I \times dt = f \int_0^T V_p \times I \times dt,
\]

where \(V_p\) is the pulse voltage, \(I\) is the current, and \(P\) is the pulse discharge power in W.

To better compare the efficiency of energy use, we calculated the energy yield (EY), as shown in Eq. (2) [5]:

\[
EY = \frac{C_0 \times V 	imes R \times 1000}{P \times T}
\]

where \(C_0\) is the initial concentration in mg/L, \(V\) is the volume of treated water in L, \(R\) is the removal efficiency, \(T\) is the elapsed time in h, and \(EY\) is the mass of pollutants removed per unit of power consumption in mg/kWh.

2.4.3. Analysis of electric energy per order (EEO) and operating cost

To eliminate the influence of pollutant concentration, the electric energy per order (EEO) figure of merit was used [30]. This figure of merit is based on the first-order kinetics for the elimination of pollutants. The EEO (kWh/L) value is calculated as Eq. (3):

\[
EEO = \frac{P \times T}{1000 \times V \times \log(C_0/C_f)}
\]

where \(P\), \(V\), \(T\) and \(C_0\) have the same definitions as in Eq. (1) and Eq. (2) and \(C_f\) is the final concentration in mg/L. The total removal rate of GCs was calculated on the basis of molar mass elimination with weighted average and calculated by the following formula Eq. (4) [31]:

\[
X = \frac{w_1x_1 + w_2x_2}{w_1 + w_2}
\]

where \(X\) (%) is the overall removal, \(w_1\) and \(w_2\) are the HC and BT amounts (mol), respectively, and \(x_1\) and \(x_2\) are the removal percentages of HC and BT, respectively.

3. Results and discussion

3.1. Performance of PBCD-based systems on GC removal and sterilization

PBCD, PBCD/ACF, and PBCD/Fe-ACF systems are effective in GC removal (Fig. 2). The removal rates of GCs in PBCD-based systems were ranked as PBCD/Fe-ACF > PBCD/ACF > PBCD. At a discharge power of 57.5 W, the removal efficiencies of HC and BT at 2 h were 99% and 71% in the PBCD (Fig. S4), respectively. However, the removal effect of GC within 1 h under low power conditions is not ideal. With the addition of ACF or Fe-ACF, the removal efficiencies of HC and BT at 1 h increased to 77% and 52% in the PBCD/ACF and 94% and 81% in the PBCD/Fe-ACF, respectively, at a lower discharge power of 34.8 W. Moreover, the energy yields of the PBCD/ACF and PBCD/Fe-ACF treatments were 1.3 and 2.1 times higher than those of the mono-PBCD treatment, respectively (Fig. 2c). The synergy effect between PBCD and ACF or Fe-ACF is confirmed by calculating the synergy factor (SF), and the formula is as follow [32]:

\[
SF = \frac{k_{A,B}}{k_A + k_B}
\]

where \(k_{A,B}\) is the rate constant of coupling system of A and B; \(k_A\) and \(k_B\) are the rate constants of sole A and sole B systems, respectively. Through the pseudo-first order rate constant provided in SI (Table S4), it can be known that the SF were all >1, indicating that synergistic effect in PBCD/ACF system can be established. The addition of ACF can provide adsorption surface area for GCs to prolong the contact time and contact area of the active species with contaminants [33,34]. The iron introduced by Fe-ACF could react with the \(\text{H}_2\text{O}_2\) generated during discharge, leading to increasing active species generation [33,34].

Considering the GC concentration in range of \(\mu\)g/L in actual HWW [4], we used the best experimental parameters obtained above to treat GC at initial concentration of 2 \(\mu\)g/L. As shown in Fig. 3, compared to the GC degradation rate at initial concentration of 50 mg/L, the GC degradation was more rapid at initial GC concentration of 2 \(\mu\)g/L, indicating that the PBCD-based methods were also effective in realistic conditions (Fig. 3). Besides, in PBCD/ACF and PBCD/Fe-ACF systems, GC concentration declined rapidly in the first 10 min. The reason may be that the ACF dose of 1 g/L was far greater than the requirement for pollutant removal at low initial concentrations (2 \(\mu\)g/L). The added ACF could quickly adsorb the GCs in the solution, leading to a rapid GC removal. Then, the PBCD could degrade the remaining GCs adsorbed on ACF and achieve continuous GC concentration decrease.

In addition, all three PBCD-based systems achieved effective sterilization (Fig. 4). The OD_{590} of E. coli bacteria gradually declined with increasing treatment time (Fig. 4a). Fig. 4b shows representative images of agar plates on which E. coli cells were grown directly after being treated with the PBCD for different periods of time. After 60 min of treatment, the number of bacteria reached \(10^2\) (CFU/mL), and an approximately 7 log_{10} reduction in bacterial concentration was observed (Fig. 4).

Furthermore, the bacteria at the phylum and genus levels in actual HWW before and after PBCD treatment were analysed (Fig. 4c). All values for bacteria at the genus rank indicate a reduction of abundance after PBCD treatment: Pseudomonas (Control 10.12%, PBCD 1.06%), Trichococcus (Control 26.56%, PBCD 16.99%), Hydrogenophaga (Control 3.67%, PBCD 0.76%), Sphaerotilus (Control 20.77%, PBCD 0%), Novosphingobium (Control 2.95%, PBCD 0%), Acidovorax (Control 2.35%, 

![Fig. 2. Effects of different PBCD-based methods on (a) HC and (b) BT removal; (c) variations of GC rate constant and energy yield by different PBCD-based methods (P_{PBCD} = 49.7 W, P_{PBCD/ACF} and P_{PBCD/Fe-ACF} = 34.8 W, Fe-ACF dosage = 1 g/L, iron loading ratio = 1%, gas velocity = 4 L/min).](image-url)
Fig. 3. Degradation of HC (a) and BT (b) during PBCD-based treatments (initial GC concentration = 2 μg/L, \( P_{\text{PBCD}} = 49.7 \) W, \( P_{\text{PBCD}/\text{ACF}} \) and \( P_{\text{PBCD}/\text{Fe-ACF}} = 34.8 \) W, Fe-ACF dosage = 1 g/L, iron loading ratio = 1%, gas velocity = 4 L/min).

Fig. 4. (a) Plasma deactivation of E. coli bacteria; (b) E. coli agar culture diagram of different PBCD treatment time; (c) phylum level and genus level distribution of bacteria communities in HWW before and after PBCD treatment (\( P_{\text{PBCD}} = 49.7 \) W, \( P_{\text{PBCD}/\text{ACF}} \) and \( P_{\text{PBCD}/\text{Fe-ACF}} = 34.8 \) W, Fe-ACF dosage = 1 g/L, iron loading ratio = 1%, gas velocity = 4 L/min).
Flavobacterium (Control 2.4%, PBCD 0%). Pseudomonas is a gram-positive bacterium with very low requirements for survival. It is one of the main causes of nosocomial infections worldwide, especially respiratory tract infections, surgical wound infections, gastrointestinal infections, etc. [35]. Flavobacterium is the main pathogen of lung disease [36], and Sphaerotilus is the culprit of sludge bulking in wastewater [37]. All the above data indicate that PBCD-based treatments are effective in sterilization. It has been proven that reactive nitrogen radicals (RNS) and reactive oxygen radicals (ROS) produced by NTP can disrupt cells and their contents, leading to bacterial inactivation or even death [35,38]. What played a decisive role will be discussed in the following sections.

3.2. Functional radicals during PBCD-based treatments

By detecting the emission spectrum of the PBCD reactor with OES, a series of RNS and ROS were observed [17,25]. RNS mainly refer to the strong emission of the second positive ion system of N₂ molecules (N₂(C-B)) at 300–400 nm [17]. NOy bands in the range of 200–300 nm also appeared [17]. These excited metastable free radicals collide with microbial cells in the solution, causing the cell membrane to deform and malfunction, which eventually cause perforation [25]. In addition, the charged electrons and ions will collide with the GC molecules in the solution, breaking chemical bonds and completing the degradation of GCs [25].

Band OH(A-X) (Fig. 5a) was observed at 306–312 nm [17,25]. The emissions at 426 nm and 777.3 nm were related to radiative oxygen [25], and the first negative system O₂ (1) in the range of 500–700 nm [17] was also observed. These emissions indicated the generation of ROS during discharge. The slow combustion of oxygen atoms or free radicals released by the PBCD-based system can corrode microbial cells atom by atom [39]. In the presence of oxygen free radicals, a series of oxidation reactions would occur in the PBCD-based system, which could produce oxidizing substances, including •O₂−, •OH and ¹⁰₂ radicals, as shown in Eqs. (6)–(11) [40–43].

\[
\begin{align*}
\text{O}_2 + \text{e}^{-} & \rightarrow 2\text{•OH} \quad \text{(6)} \\
\text{O}_2 + \text{e}^{-} & \rightarrow \text{•O}_2^{-} \quad \text{(7)} \\
\text{•O} + \text{H}_2\text{O} & \rightarrow \text{•OH} \quad \text{(8)} \\
\text{•O} + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{O}_2 \quad \text{(9)} \\
\text{•O}_2^{-} + \text{H}_2\text{O}_2 & \rightarrow \text{•OH} + \text{H}_2\text{O} \quad \text{(10)} \\
\text{•O}_2^{-} + \text{•OH} & \rightarrow ²\text{O}_2 + \text{•OH} \quad \text{(11)}
\end{align*}
\]

The EPR result (Fig. 5b) with characteristic DMPO-OH signals (typical peaks with a ratio of 1:2:2:1) [44] further confirmed the existence of •OH during PBCD-based treatments (Fig. 5a). The spectral lines of the three spin adducts (DMPO-OH, DMPO-H and DMPO-NH₂) were superimposed, as shown in Fig. 5b. With the addition of ACF and Fe-ACF, the signal peaks of DMPO-OH, DMPO-H and DMPO-NH₂ were enhanced, indicating increased ROS and RNS [45,46] by combining the PBCD with ACF and Fe-ACF.

Since the reaction rate of DMPO and •O₂− (<10² M⁻¹·s⁻¹ at pH 7) is 7 orders of magnitude lower than that of DMPO and •OH (10⁹ M⁻¹·s⁻¹), the EPR measurement cannot directly confirm the existence of •O₂− [38]. To verify the role of different active species, BQ, TBA, and DABCO were added into PBCD-based systems as model scavengers for •O₂−, •OH and ¹⁰₂ radicals, respectively [47–49]. The GC removal efficiencies and rate constants decreased with the addition of BQ, DABCO, and TBA, indicating that •O₂−, ¹⁰₂ and •OH radicals were essential in GC removal during PBCD-based treatments (Fig. 5c and d). With the addition of sufficient BQ, DABCO, and TBA, the removal rate of HC decreased by 80%, 76%, and 48%, while the BT removal rate decreased by 46%, 18%, and 73%, respectively (Fig. 5c and d, Fig. S5, and Table S5). The inhibition rates of •O₂−, •OH and ¹⁰₂ on HC removal were ranked as

![Fig. 5. (a) Emission Spectrometer of PBCD of aqueous solution; (b) DMPO spin-trapping EPR spectra recorded in the PBCD-based systems and simulated data of •OH, H and NH₃ captured by DMPO; variations of kinetic rate constants and inhibition rate on (c) HC and (d) BT as a function of BQ, TBA, and DABCO (P_{PBCD} = 49.7 W, P_{PBCD/ACF} and P_{PBCD/Fe-ACF} = 34.8 W, Fe-ACF dosage = 1 g/L, iron loading ratio = 1%, gas velocity = 4 L/min).]
•O₂ > •O₂, while for BT, the inhibition rates were ranked as •OH > •O₂ > •O₂ (Fig. 5b and c). This difference can be attributed to the difference in the structure of HC and BT (Table 1). Compared with HC, BT has a cross-conjugated ketene (C-1/C-2) in ring A, a fluorine atom at the C-9 position in ring B, and a methyl group at the C-16 position in ring D. The stability of BT was higher than that of HC [50]. As •O₂ and •O₂ have a shorter lifespan than •OH [38], their reactivities with BT were lower than those with HC.

3.3. Cooperative interaction between ACF or Fe-ACF and the PBCD system

The great advantages of PBCD/ACF over the sole PBCD can be attributed to the following two reasons. On the one hand, the addition of ACF can provide adsorption surface areas for GCs to prolong contact time and contact area of the active species with contaminants and bacteria [25,51]. During sole ACF treatment, the adsorption process of HC and BT to ACFs fitted into the Langmuir model (Text S4) with R² values above 0.92 (Fig. S6a and b), indicating that the adsorption of GCs occurred at specific homogeneous positions on the surface of ACF [52]. In addition, the pseudo-second-order model was more consistent with the adsorption kinetics of GC on ACF (Fig. S6c and d, Text S4 and Table S6), indicating that the adsorption of GCs by ACF was mainly chemical adsorption through sharing or electron exchange [53]. On the other hand, the adsorption and catalytic sites on the ACF surface can be increased and regenerated by plasma-generated active species in situ [33] during PBCD/ACF treatment, thus improving the adsorption and catalytic degradation efficiency of GCs and bacteria. The axial groove of ACFs became relatively smooth with little ash attached after PBCD/ACF treatment (Fig. 6a and b), indicating that the ash material originally attached to the ACF surface or blocked in the trench was etched by high energy electrons. Correspondingly, the specific surface area (S_{BET}) and pore volume (V) of ACFs after discharging for 60 min increased from 1516.14 to 1669.76 m²/g and 0.6203 to 0.6795 cm³/g, respectively (Table S7), indicating an obvious increase in the specific surface area of ACFs and ACF adsorption capacity during discharge [54]. In addition, the aperture and surface functional groups did not change significantly before and after discharge (Fig. 6c and d), proving that plasma discharge did not damage the structure of the ACFs.

The significant enhancements observed in the PBCD/Fe-ACF system could be attributed to the following reasons. First, iron modification had positive effects on ACF adsorption performance (Table S7). After modification, S_{BET}, V, and average pore diameter (r) of iron-modified ACF increased from 1516.41 to 1757.81 m²/g, 0.6203 to 0.8119 cm³/g, and 8.181 to 9.237 nm, respectively (Fig. 7a and Table S7). Second, the Fe²⁺ introduced by Fe-ACF could react with the H₂O₂ generated during discharging, leading to increasing ROS generation [34]. ROS play an important role in the process of bacterial inactivation [25]. After modification by iron, newly formed Fe-O (530 cm⁻¹) tensile vibration (attributed to the bending of the FeO(OH) groups [52]) was observed in the FTIR spectra of the ACF surface (Fig. 7b), proving that iron was successfully loaded on the ACF surface. During discharge, the iron on the ACF was partly desquamated and agglomerated in the grooves of the ACF (Fig. 7c and d), indicating the reaction of reactive species with the iron on the ACFs. In section 3.2, we confirmed that more free radicals were indeed generated in the PBCD/Fe-ACF system through the EPR signal peak (Fig. 5b). To maintain a constant catalytic performance of Fe-ACF, reloading of iron and ACF regeneration should be considered in practical applications [49]. Third, the plasma-generated activated species could change the chemical structures and increase the oxygen-containing functional groups on the Fe-ACF surface in situ [55], increasing the catalytic sites on the Fe-ACF surface (Fig. 7b). After discharging, the C = O (1500–1900 cm⁻¹) stretching vibration became frequent, and the stretching vibration of the C—O single bond...
generated during discharging changed the chemical structures and oxygen-containing functional groups on the Fe-ACF surface.}

3.4. Identification of GC intermediates and proposal of GC degradation pathways

According to the mass-to-charge ratio ($m/z$), the chemical formulas of the degradation intermediates of HC and BT during PBCD-based treatments are proposed (Table S8), with their extracted chromatogram and mass spectrum displayed in Fig. S7. For the sake of identified intermediates, the possible degradation pathways of HC and BT are proposed in Schemes 1 and 2 in Fig. 8, respectively. In general, oxygen addition, proton transfer, and oxidative decarboxylation occurred during HC and BT degradation, leading to the ring-opening and bond-breaking reactions of GCs (Fig. 8).

By ROS attack of cyclohexenone [57], decarboxylation of keto acids, loss of $\text{H}_2\text{O}$ [58], and transfer of protons to form a double bond [58], degradation intermediates of HC-P$_{279}$, HC-P$_{292}$, and HC-P$_{254}$ were formed (Scheme 1 in Fig. 8). Specifically, HC-P$_{310}$ was formed by the attack of $\cdot$$\text{OH}$ radicals on the aromatic ring structures [59]. Intermediates of HC-P$_{280}$ and HC-P$_{250}$ were formed after repeated oxidation and decarboxylation (Scheme 1 in Fig. 8).

By ROS oxidation, decarboxylation, and dehydration [58], BT intermediates of BT-P$_{248}$, BT-P$_{262}$, BT-P$_{276}$, BT-P$_{280}$, and BT-P$_{294}$ were produced (Scheme 2 in Fig. 8). Intermediates of BT-P$_{232}$ and BT-P$_{292}$ were obtained by oxidation of alcohol and decarboxylation of keto acid [59]. Intermediates of BT-P$_{232}$ and BT-P$_{294}$ were formed by the destruction of the C–F bond by ROS [60].

In summary, the degradation pathways of HC and BT included the replacement of F atoms with hydroxyl groups, the oxidation of alcohols into keto acids, the decarboxylation of keto acids, intramolecular cyclization, cleavage, and ester hydrolysis (Fig. 8). Our previous studies showed that decreased GC toxicity could be achieved by decreasing lipophilicity [5]. The changes in GC structures during the PBCD/Fe-ACF treatment, such as hydroxylation at C-3, defluorination at C-9 and C-6, cleavage of ring A and ring D, and de-esterification at C-18 (Fig. 8), decreased the lipophilicity of GC molecules, indicating a reduction in GC toxicity during the PBCD/Fe-ACF treatment.

3.5. Exploration of the best conditions for PBCD-based systems and analysis of economic costs

To obtain the most ideal processing conditions under each reaction system, a series of single-factor control experiments were conducted. With discharge time, discharge power, ACF dosage, and Fe$^{2+}$ loading ratio, the GC removal efficiency significantly improved (Fig. 9a and b, Fig. S4).

With the discharge power increased from 34.8 to 57.5 W, the rate constants of HC and BT increased from 0.0107 to 0.0347 min$^{-1}$ and 0.0035 to 0.0101 min$^{-1}$ (Fig. 9c and d and Table S9), respectively, in the mono-PBCD system. An increase in discharge power would increase the electric field strength of the solution, thus enhancing the dissociation, ionization, and excitation processes of gas molecules [61]. Therefore, more ROS and RNS could be generated during discharge to degrade GCs. More active substances dissolved in the water also indicates that the solution has stronger sterilization properties. However, the energy yields of HC in the PBCD system decreased with increasing discharge power from 34.8 to 57.5 W, and the energy yields of BT reached equilibrium at discharge power beyond 49.7 W (Fig. 9c and d). The increased input power leads to the loss of energy in the form of heat, which further leads to a decrease in energy yield [62]. In the process of inactivating bacteria, heat only plays a minor role, mainly relying on the contribution of highly active substances such as $\text{O}$, $\cdot$$\text{OH}$, and NO$_x$ [63]. In order to balance energy yield and GC removal rate, it is recommended to set the discharge power at 49.7 W.
the discharge power of mono-PBCD treatment to 49.7 W. At a discharge power of 49.7 W and a discharge time of 2 h, the operating cost of the mono-PBCD treatment in removing GCs was US $0.2 per litre (Table 2). Compared with the previous DBD treatment costing US $4.69 per litre [5], the mono-PBCD system obviously reduces the operating costs.

Great advantages over the mono-PBCD and single ACF treatments were observed for the PBCD/ACF system at ACF dosages of 0.5–3 g/L and discharge powers from 22.7 to 57.5 W (Fig. 9). A higher ACF dosage represented a larger reaction area and more catalytic sites [23], which enhanced GC adsorption and produced more reactive radicals to degrade GCs. The increased discharge power may initiate a larger ACF adsorption surface area and more catalytic sites on the ACF surface [64], thereby increasing the removal rate of GCs. Considering that the HC removal rate of 34.8 W was 26% higher than that of 22.7 W (Fig. 9),

Fig. 8. Proposed degradation pathways of HC (Scheme 1) and BT (Scheme 2) during PBCD-based treatments (discharge power = 34.8 W, ACF dosage = 1 g/L, iron loading ratio = 1%, gas velocity = 4 L/min, discharge time = 60 min).
34.8 W was recommended for PBCD/ACF treatment. At a discharge power of 34.8 W and ACF dosage of 1 g/L, the operating cost of the PBCD/ACF treatment in removing GCs was US $0.11 per litre, which was reduced by 45% compared with the mono-PBCD treatment (Table 2).

Iron-loading concentrations can influence GC removal efficiency and energy yield in the PBCD/Fe-ACF system (Fig. 9). The GC removal rate and energy yield increased with an increasing iron-loading ratio from 0 to 1% and then decreased with an increasing iron-loading ratio from 1 to 2%. The increase in iron loading increased the catalytic sites on the ACF surface [65]. However, when the iron loading was excessive (2%), the clogging microporous structures may have led to poor adsorption.
performance and overlapping active sites in the ACFs [66], which was harmful to GC removal. At a discharge power of 34.8 W, ACF dosage of 1 g/L, iron-loading ratio of 1%, and discharge time of 60 min, the operating cost of the PBCD/Fe-ACF system in removing GCs was US $0.05 per litre, which was 55% lower than the PBCD/ACF system (Table 2). Compared with previously reported costs (photo-Fenton is US $0.02 per litre), the PBCD/Fe-ACF system is promising in HWW treatment.

4. Conclusion

An integrated PBCD and ACF or Fe-ACF was adopted for the purification of actual HWW. PBCD-based treatments were effective in GC degradation and sterilization in HWW. The removal rates of GCs were ranked as PBCD/Fe-ACF > PBCD/ACF > PBCD. By combining the PBCD with Fe-ACF, the removal efficiency of HC and BT in HWW can reach 94% and 81%, respectively, in 60 min at 34.8 W. In addition, the abundance of bacteria in HWW was also reduced, especially bacteria from the genera Pseudomonas, Trichococcus, Hydrogenophaga, and
thereby increasing the adsorption and catalytic sites of ACF and Fe-ACF.

Sphaerotilus

Comparison of electric energy per order (E_X) and related operating cost of different processes to treat pollutants.

| Approach     | Substance          | E_X (kWh) | Operating cost (US $ L⁻¹) |
|--------------|--------------------|-----------|--------------------------|
| DBD          | glucocorticoids    | 32.28     | 4.69                     |
| DBD/CoO₂     | glucocorticoids    | 18.28     | 2.65                     |
| DBD          | 2, 4-dichlorophenol| 4.83      | 0.70                     |
| Microplasma  | organophosphorus   | 0.56      | 0.08                     |
| Microplasma  | organochlorine     | 2.56      | 0.37                     |
| Photo-Fenton | terbutryn, chlorfenvinphos | 31.47 | 4.57                     |
| Photo-Fenton | micropollutant     | 0.17      | 0.02                     |
| PBCD/ACF     | glucocorticoids    | 1.39      | 0.20                     |
| PBCD/ACF     | glucocorticoids    | 0.76      | 0.11                     |
| PBCD/Fe-ACF  | glucocorticoids    | 0.38      | 0.05                     |

* The European Union currently maintains an average industrial electricity price of US $0.15/ kWh [69].

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

This research has been co-financed by the National Natural Science Foundation of China (No. 51979039, 51708096), Shanghai Chen-Guang Program (19CG38), and the International Cooperative Projects of Shanghai Municipal Committee of Science and Technology (18230722800). All the financial supports are gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data to this article can be found in the supporting information.

Appendix B. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/jcej.2021.132845.
H. Guo, N. Jiang, H. Wang, K. Shang, N. Lu, J. Li, Y. Wu, Enhanced catalytic 
I.D. Jimenez, S. Giannakis, D. Grandjean, F. Breider, G. Grunauer, J.L.C. Lopez, J.A. 
J.R. Bolton, K.G. Bircher, W. Tumas, C.A. Tolman, Figures-of-merit for the 
J. Zhan, Y. Liu, W. Cheng, A. Zhang, R. Li, X. Li, S. Ognier, S. Cai, C. Yang, J. Liu, 
Hangbo Xu, Yupan Zhu, Mengru Du, Yuqi Wang, Siyao Ju, Ruonan Ma, Zhen Jiao, 
L. Chu, R. Zhuan, D. Chen, J. Wang, Y. Shen, Degradation of macrolide antibiotic 
Shi Gong, Yabing Sun, Ke Zheng, Guilin Jiang, Lian Li, Jingwei Feng, Degradation 
H. Guo, Peng Sun, Hongqing Feng, Haixia Zhou, Ruexue Wang, 
J.-F. Bernardet, J.P. Bowman, The genus flavobacterium, Springer New York 
S. Perez, C. Pulgarin, Unfolding the action mode of light and homogeneous vs. 
Chem. 73 (2001) 627 
Fada Feng, Jeongkwon Kim, He-Plasma Jet Generation and Its Application for E. 
W.H. Van Hulle, O. Hamdaoui, J. Vandamme, J. Van Durme, P. Surmont, F. Lynen, 
reactor, J. Hazard. Mater. 369 (2019) 611, https://doi.org/10.1016/j.jhazmat.2019.12.087. 
H. Yahia, Low-
[62] Jiaye Wen, Yuan Li, Mengyao Zhang, Baohong Guo, Guanjun Zhang, Influence of discharge types on hydrogen peroxide generation in water with/without pi film barrier, IEEE Trans. Dielectr. Electr. Insul. 26 (4) (2019) 1270–1278, https://doi.org/10.1109/TDEI.9410.1109/TDEI.2019.007994.

[63] J. Ehlebeck, U. Schnabel, M. Polak, J. Winter, T. von Woedtke, R. Brandenburg, T. von dem Hagen, K.-D. Weltmann, Low temperature atmospheric pressure plasma source for microbial decontamination, J. Phys. D. 44 (2011), https://doi.org/10.1088/0022-3727/44/1/013002.

[64] M.F.F. Pego, M.L. Bianchi, J.A. Carvalho, T. Veiga, Surface modification of activated carbon by corona treatment, An. Acad. Bras. Cienc. 91 (2019) 10, https://doi.org/10.1590/0001-3765201920170947.

[65] Tian Gu, Fengyu Gao, Xiaolong Tang, Honghong Yi, Shunzheng Zhao, Sani Zaharaddeen, Runcao Zhang, Ruijie Zhuang, Yingli Ma, Fe-modified CeMnOx/ACF catalysts for selective catalytic reduction of NOx by NH3 at low-middle temperature, Environ. Sci. Pollut. Res. 26 (27) (2019) 27940–27952, https://doi.org/10.1007/s11356-019-05976-4.

[66] Huacun Huang, Daiqi Ye, Bichun Huang, Zhengle Wei, Vanadium supported on viscose-based activated carbon fibers modified by oxygen plasma for the SCR of NO, Catal. Today. 139 (1-2) (2008) 100–108, https://doi.org/10.1016/j.cattod.2008.08.026.

[67] Muhammad Saiful Islam Khan, Na Ri Lee, Jaehwan Ahn, Ji Young Kim, Jong Hoon Kim, Ki Hyun Kwon, Yun-Ji Kim, Degradation of different pesticides in water by microplasma: the roles of individual radicals and degradation pathways, Environ. Sci. Pollut. Res. 28 (7) (2021) 8296–8309, https://doi.org/10.1007/s11356-020-11127-z.

[68] Ana Ruiz-Delgado, Melina Antonella Roccamante, Sixto Malato, Ana Agüera, Isabel Oller, Olive mill wastewater reuse to enable solar photo-Fenton-like processes for the elimination of priority substances in municipal wastewater treatment plant effluents, Environ. Sci. Pollut. Res. 27 (30) (2020) 38148–38154, https://doi.org/10.1007/s11356-020-09721-0.

[69] N. Wardenier, Z. Liu, A. Nikiforov, S.W.H. Van Hulle, C. Leys, Micropollutant elimination by O3, UV and plasma-based AOPs: An evaluation of treatment and energy costs, Chemosphere. 234 (2019) 715–724, https://doi.org/10.1016/j.chemosphere.2019.06.033.