



Peroxydisulfate activation by positively polarized carbocatalyst for enhanced removal of aqueous organic pollutants

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ABSTRACT

Multi-walled carbon nanotubes (MWCNTs)/peroxydisulfate (PDS) is a green oxidative system for abatement of aqueous organic pollutants, while the powder form and poor cycling performance of the catalyst limit its practical application. To solve these problems, fabricating a MWCNT cathode (negative polarization) to coupling carbocatalysis-driven PDS activation with electrosorption of organic pollutant was previously demonstrated to be a possible solution to these problems. To further improve the activation efficiency of PDS, positive polarization of MWCNT electrode (anode) was adapted to activate PDS for removing acyclovir and phenol in this work. Under a working voltage of 1.2 V, the MWCNT anode was more efficient than the MWCNT cathode and the non-polarized MWCNT electrode for PDS activation and removal of organic pollutants, owing to the enhanced attraction between $S_2O_8^{2-}$ anions and anode. Although the positive/negative polarization of MWCNT electrode doesn't alter the nonradical mechanism involved in MWCNTs/PDS system, theoretical calculations suggest that different polarization affect the electron configuration and oxidative capacity of activated $S_2O_8^{2-}$ bounded to MWCNTs differently, and that the adsorbed $S_2O_8^{2-}$ with stretched S–O bond and much higher oxidative capacity than that in the case of non-polarized MWCNT electrode is responsible for the MWCNTs anode, while adsorbed $S_2O_8^{2-}$ with stretched O–O bond and slightly higher oxidative capacity is responsible for the MWCNTs cathode. Finally, implications of operation parameters including electrode potential, energy cost, pH, etc. on the elimination efficiency by MWCNT anode/PDS system were investigated and the results suggest that the MWCNT anode/PDS is an efficient and economical metal-free electrochemical oxidative system for organic contaminants remediation.

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1. Introduction

The advanced oxidation processes (AOPs), which are well-known powerful techniques for abatement of organic pollutants, have been universally applied in industry (Miklos et al., 2018). In AOPs, highly reactive oxygen species (ROS) are exploited to completely mineralize organic contaminants or transform the bio-

recalcitrant organic compounds into biodegradable products prior to the bioprocessing (Chen et al., 2017; Duan et al., 2018c).

Peroxydisulfate (PDS) as a green oxidant has been widely applied for AOPs in the last two decades because the activation of PDS can generate reactive sulfate radicals ($SO_4^{\bullet-}$) which possess higher redox potential and longer lifetime than hydroxyl radicals ($OH^{\bullet}$) (Chen et al., 2018; Duan et al., 2018c). Traditionally, metal and metal oxides have been commonly employed to activate PDS due to the easy operation and high efficiency (Anipsitakis et al., 2006, 2005). Unfortunately, leaching of metal ions may happen when metallic activators are used, which may result in secondary

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pollution (Anipsitakis et al., 2005). To address this issue, developing metal-free catalysts is of great importance. Carbonaceous materials including activated carbons, carbon nanotubes (CNTs), reduced graphene oxide, mesoporous carbon, nanodiamonds, carbon aerogels and so on have been recently reported to show good catalytic activity towards PDS activation (Chen et al., 2018; Duan et al., 2018a, 2018c, 2016, 2015). However, most carbocatalysts are in the form of powder, which requires a post-treatment like filtration or high-speed centrifugation to separate and recycle the catalysts. The involvement of such post-treatment hinders the practical application of these promising carbocatalysts in abatement of organic pollutants. To overcome this disadvantage, integrating the powdery catalysts with binders to fabricate electrodes can be a potential solution. The carbonaceous electrodes can be immersed into the solution or assembled into units to activate PDS to remove organic pollutants, making the separation and recycling of carbocatalysts convenient.

Capacitive deionization (CDI), which is also known as electro-sorption, has been proposed as an energy-saving electrochemical method for removing inorganic ions and organic compounds with respect to electrolysis (Porada et al., 2013; Tang et al., 2019). Due to the suitable porous structures and electrical conductivity, carbonaceous materials are commonly utilized as CDI electrode materials (Li et al., 2009, 2018; Liu et al., 2015; Xu et al., 2016). In electro-sorption process, the applying of direct current voltage below the breakdown voltage of water (1.23 V) onto the porous electrodes can induce the quick accumulation of ions or charged organic groups in aqueous solution onto the surface of polarized electrodes, forming the so-called electric double layer. Our previous work (Nie et al., 2018) showed that enhanced removal of aniline could be achieved by using a negatively polarized multi-walled CNT (MWCNT) electrode (cathode) due to the synergistic effect between electro-sorption of organics and activation of PDS. In addition, the MWCNT cathode exhibited much better stability than the MWCNTs catalysts for aniline removal, suggesting that the continuous supply of negative charges which serve as persulfate activator may reduce the consumption of active sites in carbocatalysts. Remarkably, such an approach required much lower energy cost compared to the electrolytic activation of PDS process at platinum (Pt) cathode regarding the aniline mineralization. Thereby, utilization of polarized MWCNT electrode to activate PDS is indicated to be a potential economical and efficient technique for abatement of aqueous organic contaminants. To promote the practical application of this technique, attempts to further improve the PDS activation efficiency are necessary. Additionally, the mechanism of PDS activation at MWCNT cathode was not well-understood in our previous work, e.g., the detailed electronic structure of the nonradical ROS generated by PDS activation, which is worthy of further investigation.

It has been reported that the electro-activation of PDS can be realized by both cathodic activation and anodic activation while the efficiency and induced ROS in the two cases are different (Chen et al., 2014; Chen and Huang, 2015; Matzek et al., 2018; Song et al., 2017). For instance, Chen et al. unveiled the PDS reduction at cathodic platinum (Pt) electrode to generate $\text{SO}_4^{\bullet-}$ via one-electron transfer reaction (Chen et al., 2014; Chen and Huang, 2015). Ma and co-workers recently reported that the anodic activation of PDS at Pt electrode is more efficient than the cathodic activation and nonradical oxidation is responsible for the anodic activation (Song et al., 2017). Consequently, we speculate that higher activation efficiency of PDS and different activation mechanism may also be induced by positive polarization of MWCNT electrode (anode) compared to the MWCNT cathode. However, relevant studies are scarcely present in the literature.

Herein, removal of acyclovir, which is a typical antivirus agent, and hazardous phenol by MWCNT anode or MWCNT cathode in a

flow-between asymmetric quasi-CDI (AQCDI) unit cell were compared. The stability of MWCNT anode for PDS activation and removal of acyclovir was also studied. In addition, the influence of positive charges and negative charges at the surface of MWCNT electrode on the activation of PDS were systematically investigated and the involved activation mechanisms were unveiled by conducting control experiments using an AQCDI unit cell incorporated with ion-exchange membrane, electrochemical analyses and theoretical calculations. Finally, the corresponding energy consumption, influences of pH values, voltages, PDS concentration and background matters such as chloride ions, carbonate ions on the degradation efficiency of acyclovir were evaluated to assess the potential application of activated PDS by MWCNT anode using an AQCDI unit cell for abatements of organic contaminants in wastewaters.

2. Materials and methods

2.1. Materials

Details on the MWCNTs, chemicals and preparation of solutions use in this work can be found in Text S1.

2.2. Assembling of AQCDI unit cell

A casting method as reported in the literature was employed to fabricate MWCNT electrodes (Park and Choi, 2010). Details are described in Text S2. An AQCDI cell with similar configuration to those used in other studies (Li et al., 2009, 2018) was assembled (Fig. S1) and the details can be found in our previous work (Nie et al., 2018). For control experiments, an anion-exchange membrane (AEM) or cation-exchange membrane (CEM) with the same dimension as MWCNT electrode was placed in front of the MWCNT electrode (Fig. S1) and the assembled unit was named as AQCDI/AEM or AQCDI/CEM.

2.3. Removal of organic pollutants

Batch experiments were performed in a continuously recycling system (Nie et al., 2018) and pH of the solution of organic pollutant was not buffered unless specified. More details are provided in Text S3.

2.4. Analytical methods

A HPLC equipped with a UV detector (Elite, Eclassical3100) was used to measure the concentration of all organic pollutants. Methanol and ultrapure water were employed as mobile phases at a flow rate of 0.8 mL min^{-1} . Total organic carbon (TOC) was measured with a TOC analyzer (TOC-L CPH, Shimadzu). KI method was used to measure the concentration of PDS (Liang et al., 2008). Linear sweep voltammetry (LSV) were performed on a CHI 660E electrochemical workstation (CH Instruments Ins., Shanghai) with a three-electrode cell (see Text S4 for details). Electron paramagnetic resonance (EPR, Bruker EMXPlus-10/12) spectra were recorded to analyze the generated active radicals. The solution pH was measured by a pH meter (Leici, Shanghai).

3. Results and discussion

3.1. Comparison of organic pollutants abatement among various systems

Acyclovir and phenol were selected as the target organic pollutants to evaluate the degradation performance of polarized

MWCNT electrode-catalyzed PDS activation with the AQCDI cell. In the case of acyclovir removal (Fig. 1a), adsorption-desorption equilibrium of the organics onto MWCNT electrode was reached in 90 min and MWCNT electrode itself could adsorb a certain amount of acyclovir due to the large specific surface area ($SSA = 442 \text{ m}^2 \text{ g}^{-1}$) of MWCNTs (Nie et al., 2018). After adding PDS into the acyclovir solution, the concentration of organic compound was further decreased without the applying of voltage on the AQCDI unit cell (AQCDI/PDS/0V), ascribing to the reason that the $\text{S}_2\text{O}_8^{2-}$ ions flowing through the surface of MWCNT electrode could be effectively activated to generate ROS for oxidizing acyclovir (Guan et al., 2017). A control experiment with acyclovir oxidation by PDS alone indicated that PDS itself could hardly oxidize acyclovir. Once a constant voltage of 1.2 V was imposed on the AQCDI unit cell (connecting MWCNT electrode to the positive pole or negative pole of the power was referred as AQCDI/PDS/1.2V or AQCDI/PDS/-1.2V, respectively), quicker degradation of acyclovir was achieved with respect to the AQCDI/PDS/0V system, suggesting that the polarization of MWCNTs catalysts accelerated the abatement of organic pollutant remarkably.

To explain such enhanced performance, electrosorption of acyclovir by the AQCDI unit cell and degradation of acyclovir with a QCDI unit cell composed of two graphite sheets electrodes (g-QCDI) were studied. It was observed that a significant amount of acyclovir was removed upon positive polarization (AQCDI/1.2V) or negative

polarization (AQCDI/-1.2V) of MWCNT electrode, attributable to the reason that the dipole moment of the organic compound is increased due to the changes of surface charge-density on the C surface upon positive or negative polarization and thus enhances the π - π interaction between the aromatic rings of organic compound and the surface of MWCNT electrodes (Bayram and Ayranci, 2010). Notably, higher removal efficiency of acyclovir was achieved by AQCDI/-1.2V (67%) than AQCDI/1.2V (46%), which possibly because a small amount of cationic acyclovir may be present in the solution resulting from the partially dissociation of electron-accepting groups in acyclovir molecule under the electric field and the cationic acyclovir was attracted onto the surface of MWCNT cathode. However, graphite paper could barely adsorb the organic compound and only 10% acyclovir was degraded in 180 min by PDS activation with the g-QCDI unit cell under a voltage of 1.2 V. As known, graphite paper shows low SSA and poor catalytic activity towards PDS activation (Lee et al., 2015). By replacing one graphite paper electrode with MWCNT electrode in the g-QCDI unit cell, the higher catalytic activity and electrosorption capacity of MWCNTs endowed by the larger SSA and unique nanostructures can improve both the PDS activation efficiency and the adsorption of acyclovir, resulting in elevated degradation performance. In addition, the close interaction between the electrochemically adsorbed organic molecules and surface reactive species generated from PDS activation at the electrode facilitates the electron transport between

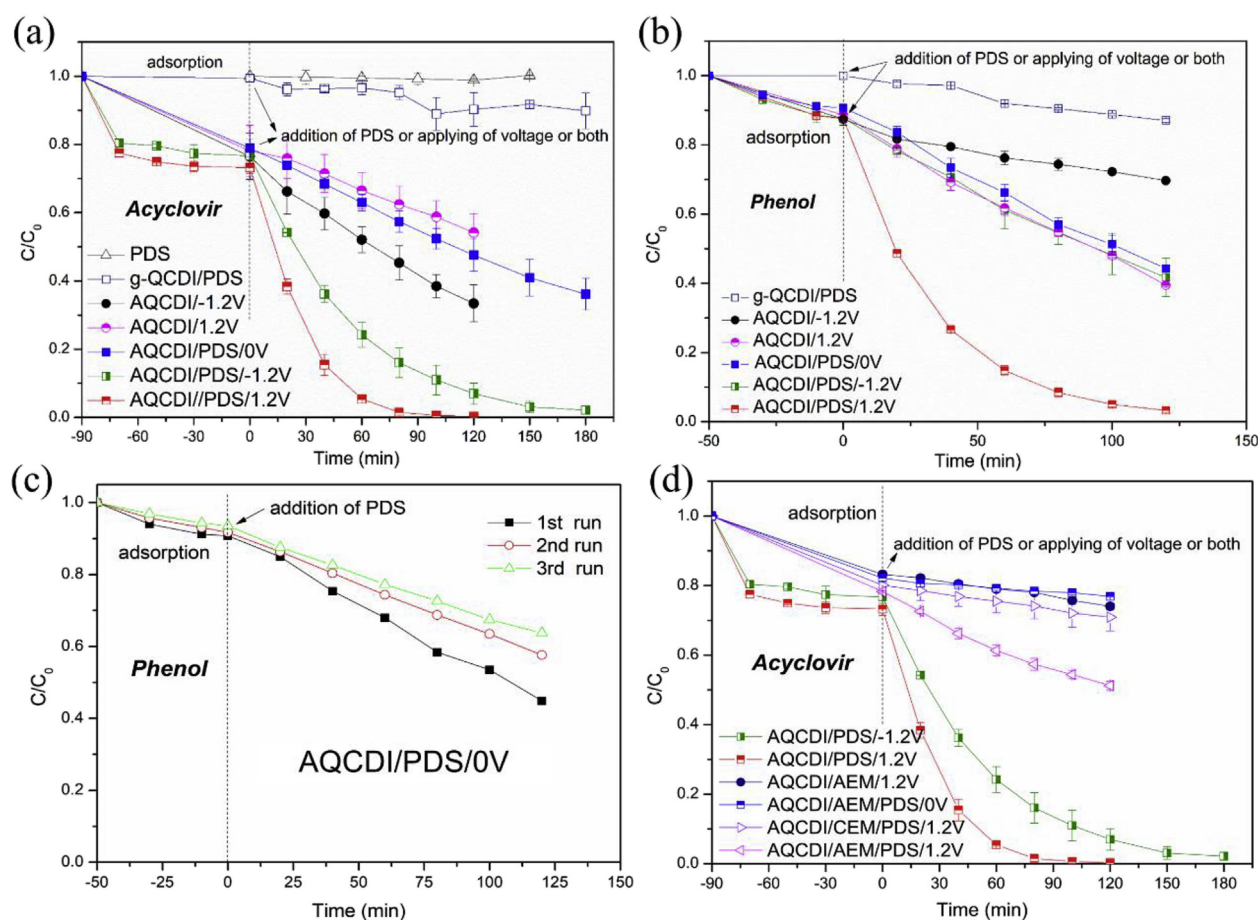


Fig. 1. (a) Removal of acyclovir by PDS alone, g-QCDI/PDS system under 1.2 V voltage, AQCDI/-1.2V system, AQCDI/1.2V system, AQCDI/PDS/0V, AQCDI/PDS/-1.2V system and AQCDI/PDS/1.2V system, respectively; (b) Removal of phenol by g-QCDI/PDS system under 1.2 V voltage, AQCDI/-1.2V system, AQCDI/1.2V system, AQCDI/PDS/0V system, AQCDI/PDS/-1.2V system and AQCDI/PDS/1.2V system, respectively; (c) Recycling performance of AQCDI/PDS/0V system for phenol removal; (d) Removal of acyclovir by AQCDI/PDS/-1.2V system, AQCDI/PDS/1.2V system, AQCDI/AEM/1.2V system, AQCDI/AEM/PDS/0V system, AQCDI/AEM/PDS/1.2V system and AQCDI/AEM/PDS/1.2V system, respectively. Conditions: $[\text{acyclovir}]_0 = [\text{phenol}]_0 = 0.45 \text{ mM}$; $[\text{PDS}]_0 = 11.1 \text{ mM}$.

them and promotes the oxidation of pollutants.

In the case of phenol removal (Fig. 1b), the adsorption-desorption equilibrium onto MWCNT electrode was reached in 50 min and around ~12% phenol was removed by adsorption. Similarly, g-QCDI/PDS/1.2V showed poor degradation performance while both AQCDI/PDS/1.2V (97%) and AQCDI/PDS/-1.2V (58%) systems exhibited higher removal efficiency than AQCDI/PDS/0V (55%), verifying that the synergistic effect between the electro-sorption of organic compound onto MWCNT electrode which was demonstrated in the control experiments and carbocatalysis-driven PDS activation could enhance the abatement of organic pollutants. Unlike acyclovir, higher removal efficiency of phenol was achieved by AQCDI/1.2V (61%) than AQCDI/-1.2V (30%), possibly because phenol molecules contain electron-donating groups which are preferentially attracted onto MWCNT anode.

Another point to note that the AQCDI/PDS/1.2V system outperformed the AQCDI/PDS/-1.2V system in both acyclovir and phenol removal. The improved performance of AQCDI/PDS/1.2V system for phenol removal can be related to the higher electro-sorption efficiency of MWCNT anode than MWCNT cathode. However, decreased electrosorptive removal of acyclovir was achieved with MWCNT anode compared to MWCNT cathode. This phenomena unveiled that the polarization of MWCNT electrode may exert influence on the PDS activation and MWCNT anode was more efficient than the MWCNT cathode for PDS activation, consistent with the previous work (Song et al., 2017). Moreover, the variations of PDS concentration in AQCDI/PDS/1.2V system and AQCDI/PDS/-1.2V system (Fig. S2) confirmed that more PDS were decomposed on the MWCNT anode. It is worth mentioning that although AQCDI/PDS/-1.2V system only showed a little higher phenol removal efficiency than AQCDI/PDS/0V system in which fresh MWCNTs were used, the performance of the former remained stable while the latter declined gradually in three consecutive tests (Fig. 1c). These results disclosed that the active sites present in MWCNTs predominantly reacted with PDS during the activation process while the charges on the surface of MWCNT cathode could assist the PDS activation when the active sites were gradually consumed in recycling tests.

It has been proposed that the during the process of anodic activation of PDS at Pt anode, $S_2O_8^{2-}$ ions firstly migrate to the anode by the coulombic force and then the electron configuration of the ions are rearranged under the influence of surface positive charges of anode, resulting in the formation of a transition state of PDS molecule bounded on the Pt anode which serves as the primary nonradical reactive species responsible for organic pollutants degradation (Song et al., 2018). To understand if the electrostatic attraction could also enhance the PDS activation at polarized MWCNT electrode, ion-exchange membranes are introduced into the AQCDI unit cell and the acyclovir degradation behaviors of the resultant unit cells were evaluated. Fig. 1d shows that the AQCDI/CEM/PDS/1.2V system only gave a total removal efficiency of ~29% while the adsorption of organic pollutant onto MWCNT electrode accounted for ~20%, revealing the low effectiveness for PDS activation. Compared to AQCDI/CEM/PDS/1.2V system, AQCDI/AEM/PDS/1.2V system gave a higher total removal efficiency of ~49%, which should arise from the reason that the cation selectivity of CEM inhibited the electro-sorption of $S_2O_8^{2-}$ ions onto the surface of MWCNT anode and thus suppressed the PDS activation. The above results demonstrated that the electrostatic attraction between PDS and MWCNT anode play an important role during the process of PDS activation at MWCNT anode. For comparison, acyclovir degradation by AQCDI/AEM/PDS/0V system and electrosorptive removal of acyclovir by AQCDI/AEM/1.2V system were also tested. As seen, AQCDI/AEM/PDS/0V system achieved a much lower removal efficiency (~23%) than AQCDI/PDS/0V system, which is likely

because that the ion-exchange membrane in front of MWCNT electrode was fouled by the organic substances (Tanaka et al., 2012) and thus hindered the permeation of PDS in the flowing solution onto the surface of MWCNT electrode, abating the carbocatalysis. Additionally, the lower electrosorptive removal of acyclovir by AQCDI/AEM/1.2V system (~26%) than AQCDI/1.2V system (~46%) suggested that the presence of ion-exchange membrane also hinders the electro-sorption of organic compound onto MWCNT electrode due to the fouling effect. As a consequence of the inhibitory effect of AEM on acyclovir electro-sorption and catalysis-driven PDS activation, decreased performance of AQCDI/AEM/PDS/1.2V system than AQCDI/PDS/1.2V system was obtained.

3.2. Quenching experiments

Methanol is popularly used as radical scavenger for both $SO_4^{\bullet-}$ and $HO^{\bullet}$ ($K_{SO_4^{\bullet-}} = 2.5 \times 10^7 M^{-1} S^{-1}$, $K_{HO^{\bullet}} = 9.7 \times 10^8 M^{-1} S^{-1}$) according to the reference (Buxton et al., 1988) and singlet oxygen (1O_2) can be scavenged by NaN_3 ($K_{^1O_2} = 1 \times 10^9 M^{-1} S^{-1}$) or furfuryl alcohol (FFA $K_{^1O_2} = 1.2 \times 10^8 M^{-1} S^{-1}$) (Chen et al., 2018). To discern the primary reactive species during MWCNTs powders-catalyzed PDS activation and polarized MWCNTs-catalyzed PDS activation, the scavengers were separately added into the aqueous solution using acyclovir as the model compound. FFA/ NaN_3 was used here because 1O_2 has been recently reported as the primary ROS in PDS activation by CNTs and biochar (Cheng et al., 2017; Yin et al., 2019; Zhu et al., 2018). Fig. 2a and b shows that the presence of methanol and FFA/ NaN_3 barely inhibited the degradation of acyclovir, suggesting that both MWCNTs/PDS and AQCDI/PDS/1.2V oxidative systems are not relied on either free radicals or 1O_2 during the PDS activation process. EPR measurements further supported that neither free radicals nor 1O_2 was involved in the MWCNTs/PDS system (Fig. S3). Hence, surface-bounded activated PDS in a metastable state is proposed to dominate the oxidation in the above two systems via a nonradical manner to attack the organic substance by electron abstraction, in accordance with the reported works (Guan et al., 2017; Song et al., 2017; Zhang et al., 2014).

Quenching experiments with AQCDI/PDS/-1.2V system (Fig. 2c) revealed that nonradical oxidation pathway was also responsible for the activation of PDS at the MWCNT cathode, quite differing from the commonly reported sulfate radicals-dominated cathodic activation of PDS process which was stimulated by electrolysis at high working voltages (Chen et al., 2014; Chen and Huang, 2015). It would be interesting to investigate if the increase of voltage could lead to the generation of free radicals from PDS activation at MWCNT cathode. First, a voltage of -2 V was applied to the MWCNT electrode and degradation efficiency of acyclovir was measured. Then quenching experiment with 1 M methanol under the same voltage was conducted. After that, we repeated the two experiments on the same electrode. As shown in Fig. 2d, although acyclovir degradation in the two quenching experiments was partially inhibited compared with two control experiments without methanol, the performance of AQCDI/PDS/-2V system gradually decreased after the first two cycles. Hence, the increase of working voltage for cathodic activation may not induce a radical system but resulted in decay of performances. This could possibly be attributed to the faradaic reactions occurred at carbon outer layer which gave rise to partial surface oxidation when a high voltage was applied (He et al., 2016).

3.3. Electrochemical analysis

To illustrate the involved mechanism for AQCDI/PDS/1.2V and AQCDI/PDS/-1.2V systems, LSV measurement was performed to analyze the electron transfer between the reactants and electrode

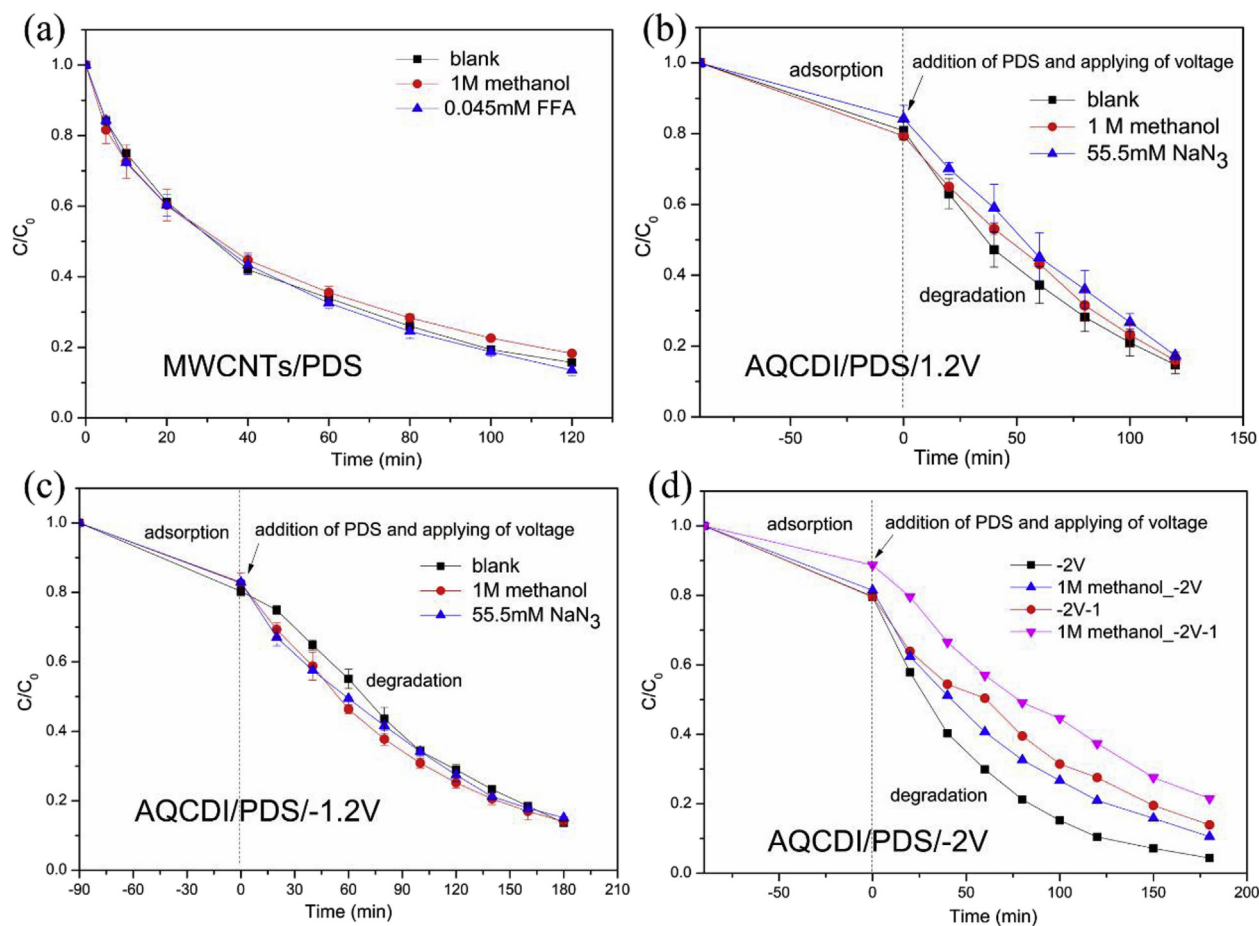


Fig. 2. (a) Influence of addition of 1 M methanol and 0.045 mM FFA on the degradation of acyclovir by MWCNTs/PDS system and control experiment (red circle). Conditions: $[\text{acyclovir}]_0 = 0.45 \text{ mM}$; $[\text{PDS}]_0 = 5.55 \text{ mM}$; Influence of addition of 1 M methanol and 55.5 mM NaN_3 on the degradation of acyclovir by (b) AQCDI/PDS/1.2V system and (c) AQCDI/PDS/-1.2V system and control experiments. Conditions: $[\text{acyclovir}]_0 = 0.45 \text{ mM}$; $[\text{PDS}]_0 = 5.55 \text{ mM}$; (d) Influence of addition of methanol on the degradation of acyclovir by AQCDI/PDS/-2V system in different cycles. Conditions: first cycle without addition of methanol (black square); first cycle with addition of 1 M methanol (blue triangle); second cycle without addition of methanol (red circle); second cycle with addition of 1 M methanol (pink triangle); $[\text{acyclovir}]_0 = 0.45 \text{ mM}$; $[\text{PDS}]_0 = 11.1 \text{ mM}$. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

surface. Fig. 3a depicts a minor current increase with the addition of acyclovir or PDS alone, implying the negligible electron transfer between PDS or acyclovir and MWCNT electrode. However, the

current increased slightly once the scanning voltage was above 1.05 V when acyclovir and PDS were simultaneously present, indicating that oxidation of acyclovir occurred on the surface of carbon

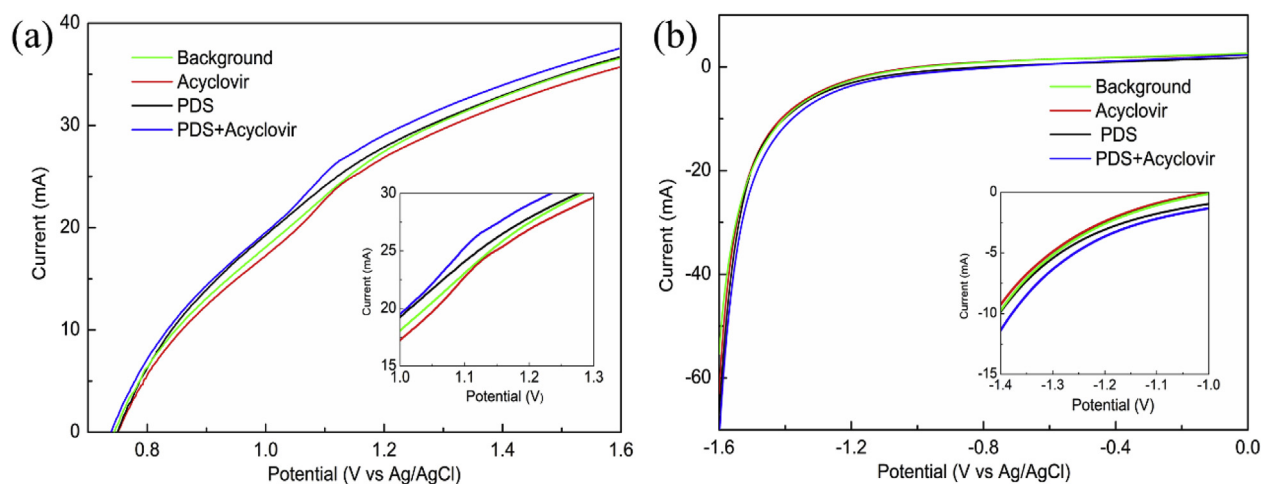


Fig. 3. Linear sweep voltammetry of PDS and acyclovir at MWCNT electrode with (a) positive and (b) negative scanning voltage in 0.1 M Na_2SO_4 electrolyte. Sweep rate = 0.01 V s^{-1} ; $[\text{acyclovir}]_0 = 0.45 \text{ mM}$; $[\text{PDS}]_0 = 11.1 \text{ mM}$.

electrode. Therefore, we speculate that when $\text{S}_2\text{O}_8^{2-}$ ion was adsorbed onto the MWCNT anode, it was transformed into an activated state stimulated by the electric charge at the MWCNT electrode without decomposed into sulfate radicals while the activated PDS could react with the organic molecules when they were also present in the solution to produce sulfate ions, which gave rise to a slight increase of current. An identical tendency was present in Fig. 3b when a negative potential was applied to the MWCNT electrode, revealing the same activation mechanism involved at the MWCNT cathode. The similar LSV measurements were also observed for EC/Ti/Pt_anode/PDS, CNT/PDS and graphitized nanodiamonds/PDS (G-ND/PDS) systems (Lee et al., 2016, 2015; Song et al., 2017). Ma et al. recently proposed that LSV may not be a suitable characterization method for identifying the mechanism of PDS activation in CNT/PDS or G-ND/PDS based nonradical systems, as the involved PDS activation is a heterogeneous process instead of an electrochemical process (Song et al., 2017). Our results in this work demonstrated that the PDS could be electrochemically activated by nanocarbon electrode, which contributed to the signals in the LSV measurements, supporting the Ma's perspective.

3.4. Theoretical investigation on the PDS activation by charged MWCNT electrode

Although the above results indicated that the activation pathway of PDS by MWCNTs was not altered by the polarization of MWCNTs, the influence of positive or negative surface charges of MWCNTs on the structures and electronic states of the activated PDS is unknown. To this end, density functional theory (DFT) modeling, which has been widely employed to elucidate the reactions occurring at the surface of carbonaceous electrodes as well

as the intricate interaction between persulfates and carbocatalysts (Chen et al., 2018; Duan et al., 2018a, 2016), was adopted to simulate the possible adsorption configurations of $\text{S}_2\text{O}_8^{2-}$ anion adsorbed onto the surface of polarized CNT electrode under different electrical fields (upward positive electric field denotes anode, while downward negative electric field denotes cathode as shown in Fig. 4). Details of the modeling are provided in Supplementary Materials (Text S5). Corresponding adsorption energy, the quantity of atonic charge on $\text{S}_2\text{O}_8^{2-}$ anion by Hirshfeld analysis (Q), length of O–O bond ($l_{\text{O-O}}$), S–O bond ($l_{\text{S-O}}$) of the most stable structures for adsorbed $\text{S}_2\text{O}_8^{2-}$ anion were summarized in Table 1. Note that SWCNT was adopted to simplify the model structure because the electronic properties of perfect MWCNTs are rather similar to those of perfect SWCNTs and the number of CNT walls slightly affects the adsorption (Baughman et al., 2002; Wang et al., 2010). In addition, an electric field with different directions was applied to simulate the effect of the polarized electrode in the DFT calculations.

Table 1

The calculated adsorption energy (E_{ads}), the quantity of atonic charge on $\text{S}_2\text{O}_8^{2-}$ anion by Hirshfeld analysis (Q), O–O bond length ($l_{\text{O-O}}$) of SO_4-SO_4 and S–O bond length ($l_{\text{S-O}}$) of SO_3-SO_5 in $\text{S}_2\text{O}_8^{2-}$ anion from different adsorption configuration and chemical potential (μ) and global electrophilicity index (ω) of adsorbed $\text{S}_2\text{O}_8^{2-}$ anion on SWCNT under different electrical field.

	F (au)	E_{ads} (eV)	Q (e)	$l_{\text{O-O}}$ (Å)	$l_{\text{S-O}}$ (Å)	μ	ω
CNT cathode	−0.005	−1.5	−1.66	1.477	1.751	2.530	1.606
	−0.003	−2.1	−1.55	1.456	1.772	2.064	1.034
	−0.001	−2.72	−1.44	1.444	1.787	1.624	0.629
Neutral CNT	0	−2.78	−1.37	1.428	1.812	1.448	0.501
CNT anode	+0.001	−3.41	−1.32	1.414	1.832	−2.034	5.783
	+0.003	−4.16	−1.19	1.403	1.839	−3.858	52.225
	+0.005	−4.97	−1.05	1.360	1.925	−5.836	234.889
	+0.007	−5.85	−0.93	1.337	1.978	−8.936	140.322

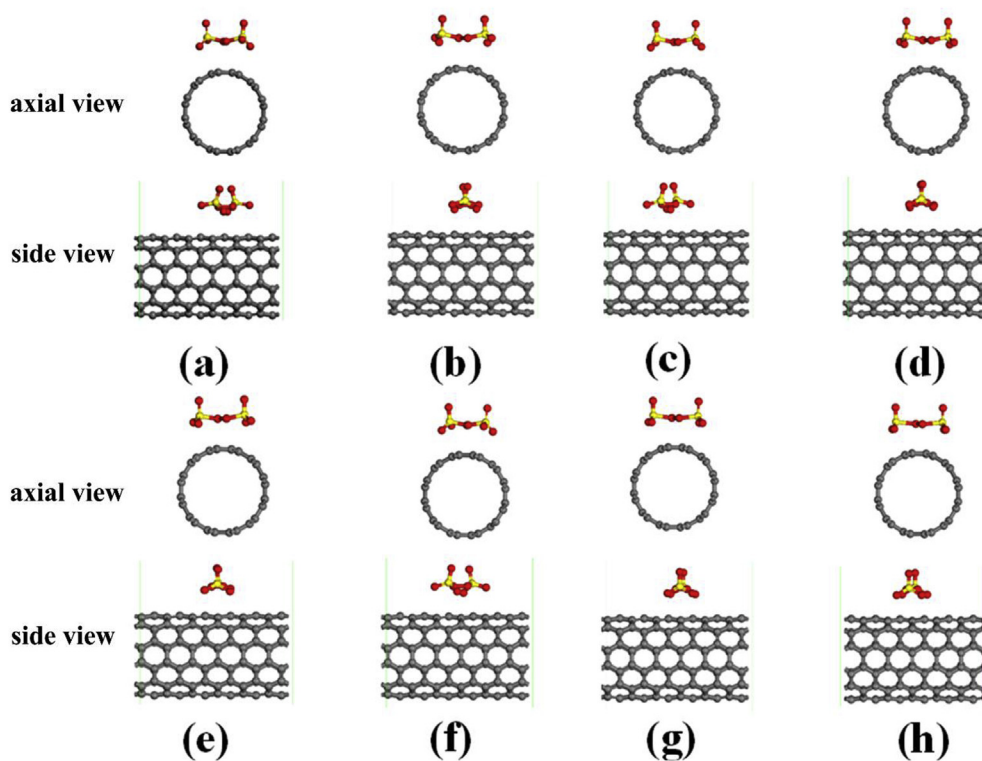


Fig. 4. The structure of $\text{S}_2\text{O}_8^{2-}$ anion adsorbed on CNT electrodes in different electronic field: (a) -0.005 au ($1 \text{ au} = 5.14 \times 10^{11} \text{ V m}^{-1}$), (b) -0.003 au, (c) -0.001 au, (d) 0 au, (e) $+0.001$ au, (f) $+0.003$ au, (g) $+0.005$ au and (h) $+0.007$ au. The gray, yellow and red balls are carbon, sulfur, and oxygen respectively. The positive electric field is defined as from the bottom to the top, while the negative electric field is the opposite. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

However, the intensity in the DFT calculations was different from that in experiments. The intensity of the electric field (F) was adopted in the range of 10^{-3} au ($1 \text{ au} = 5.14 \times 10^{11} \text{ V m}^{-1}$) as most of DFT works used in this work (Ao and Peeters, 2010; Wu et al., 2014), and the much higher F in simulation than that in experiment was used to compensate for a short time in DFT works (Xu and Chen, 2018). Herein, we focused on the effects of the trend of the F as well as its direction on the adsorption of PDS.

When SWCNT was negatively polarized (under a negative electric field), the calculated E_{ads} decreased and the absolute value of Q increased gradually with the rise of F compared to neutral SWCNT, suggesting that the interaction and charge transfer between $\text{S}_2\text{O}_8^{2-}$ anion and SWCNT was suppressed. This should be ascribed to the reason that the coulombic repulsive force between $\text{S}_2\text{O}_8^{2-}$ anion and SWCNT cathode weakens the interaction between them. However, the $I_{\text{O-O}}$ of $\text{S}_2\text{O}_8^{2-}$ anion gradually increased with the electrical field accompanying with the decrease of $I_{\text{S-O}}$ with respect to the case of neutral SWCNT, indicating that the surface negative charges on SWCNT could induce the further stretch of O–O bond but contraction of S–O bond in the electron-enriched $\text{S}_2\text{O}_8^{2-}$ anion. Especially when an electrical field of -0.001 au was imposed on SWCNT electrode, the E_{ads} decreased a little while the O–O bond was elongated significantly, showing that negative polarization of MWCNT with a small electrical field favors the PDS activation, consistent with our experimental results. Such activated PDS with longer O–O bond than that in the case of neutral SWCNT may possess stronger oxidizing ability for organic pollutants, thus enhancing the degradation performance. Particularly, it was found that the O–O bond was cleaved after charging $-3e$ in the structure optimization (Fig. S4), which agrees with the literature reporting the generation of $\text{SO}_4^{\bullet-}$ from cathodic activation of PDS during electrolysis process (Chen et al., 2014; Zeng et al., 2016). Thereby, the experimental evidences and DFT calculations illustrated that negative polarization of MWCNT electrode could further stretch the O–O bond of surface-bounded activated PDS and facilitate the electron transfer from MWCNT cathode to $\text{S}_2\text{O}_8^{2-}$ anion, which boost the elimination of organic pollutants.

In the case of SWCNT anode, the derived E_{ads} improved with F and these values were much higher than those obtained in the cases of both neutral SWCNT and SWCNT cathode. The higher E_{ads} obtained for SWCNT anode confirms that the electrostatic attraction between $\text{S}_2\text{O}_8^{2-}$ anion and SWCNT anode could improve the interaction between them and thus the activation efficiency of PDS, in accordance with the experimental results. Meanwhile, the electron transfer between $\text{S}_2\text{O}_8^{2-}$ anion and SWCNT anode was increased with F as the Q absolute value was reduced gradually. We deduced that changing the polarization of CNT from negative to positive induced the reverse of the charge density on CNTs, which rendered the positively polarized CNT electron-deficient (see Fig. S5), and such CNT of electron deficiency could attract the electrons in $\text{S}_2\text{O}_8^{2-}$ anion and may improve the electron transfer between the organic pollutant and surface-bounded activated PDS via a nonradical pathway. Surprisingly, we discovered that the $I_{\text{S-O}}$ of $\text{S}_2\text{O}_8^{2-}$ anion was raised remarkably while the $I_{\text{O-O}}$ was reduced with the electrical field compared to neutral SWCNT, which opposite to the tendency in the case of SWCNT cathode. This phenomena implies that negative charges and positive charges on the surface of MWCNT electrode have different influences on the electronic configuration of the activated PDS and the interaction between $\text{S}_2\text{O}_8^{2-}$ anion and SWCNT anode mainly affected the electron arrangements of S–O bond in activated PDS.

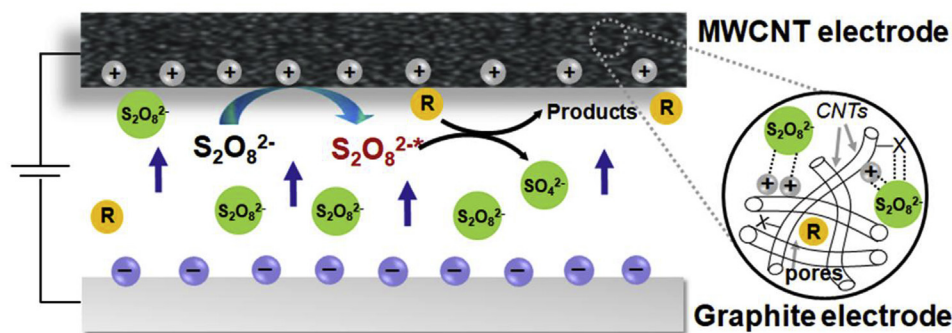
Furthermore, for the purpose of comparing the oxidative capacity of the three kinds of activated $\text{S}_2\text{O}_8^{2-}$ anions, the chemical potential (μ) and global electrophilicity index (ω) of adsorbed $\text{S}_2\text{O}_8^{2-}$ which are considered as indicators of the oxidative capacity of

activated $\text{S}_2\text{O}_8^{2-}$ anions (the higher μ and ω mean the higher oxidative capacity) under different F were also calculated (see Text S5 and Table S1 for calculation details) and listed in Table 1. As displayed, both the calculated μ and ω of adsorbed $\text{S}_2\text{O}_8^{2-}$ anion in the case of SWCNT anode were higher compared to the case of neutral SWCNT and these values ascended dramatically with the raised F, indicating the remarkable increase of electronegativity of adsorbed $\text{S}_2\text{O}_8^{2-}$ anion when CNT was positively polarized. This observation could be ascribed to the reason that the losses of electrons lead to more molecular orbitals in $\text{S}_2\text{O}_8^{2-}$ anion and thus the energy of LUMO of $\text{S}_2\text{O}_8^{2-}$ anion adsorbed onto SWCNT anode was sharply declined compared to the $\text{S}_2\text{O}_8^{2-}$ anion adsorbed onto neutral SWCNT. Based on the above results, it was deduced that the activated $\text{S}_2\text{O}_8^{2-}$ anion with further stretched S–O bond bounded to MWCNT anode exhibited much higher oxidative capacity than that bound to neutral MWCNT, which could enhance the degradation of organic pollutants by AQCDI/PDS/1.2V system. In the case of SWCNT cathode, the derived μ and ω of adsorbed $\text{S}_2\text{O}_8^{2-}$ anion under different F were also increased relative to the case of neutral SWCNT while these values were not as high as those obtained for SWCNT anode, implying a little higher oxidative capacity of the activated $\text{S}_2\text{O}_8^{2-}$ anion with further stretched O–O bond.

Combining the experimental and theoretical results, it is demonstrated that both the negative and positive polarization of MWCNT electrode can affect both the electronic state and oxidative capacity of activated PDS bounded to the surface of non-polarized MWCNTs and enhance the PDS activation, but they exert different influences on activated PDS. The negative polarization mainly results in the stretch of O–O bond and a slight increase of oxidative capacity of activated PDS while positive polarization can elongate the S–O bond in activated PDS and improve its oxidative capacity dramatically. In addition, compared with negative polarization, the positive polarization of MWCNT electrode promotes the adsorption of $\text{S}_2\text{O}_8^{2-}$ anions onto MWCNT anode due to the electrostatic attraction force, consequently improving the PDS activation efficiency and the removal of organic pollutants. Possible mechanism of removal of organic pollutants by AQCDI/PDS/1.2V system was proposed in Scheme 1. First, $\text{S}_2\text{O}_8^{2-}$ ions and organic molecules are co-adsorbed onto the surface of MWCNTs by the electrostatic field. Then the length of S–O bond in adsorbed $\text{S}_2\text{O}_8^{2-}$ is stretched by the active sites and $\text{S}_2\text{O}_8^{2-}$ transfers electrons to the surface of MWCNTs, turning the $\text{S}_2\text{O}_8^{2-}$ into an activated state. The activated $\text{S}_2\text{O}_8^{2-}$ ($\text{S}_2\text{O}_8^{2-*}$) manifests a strong oxidative capacity (Lee et al., 2016; Zhang et al., 2014). Due to the close interaction of activated PDS/carbon complex and organic molecules on the MWCNT electrode, organic molecules can be efficiently oxidized to donate electrons, and $\text{S}_2\text{O}_8^{2-*}$ is converted to $\text{SO}_4^{\bullet-}$ and then released to the bulk solution. Due to the oxidation and mineralization of the adsorbed organic compound, organic molecules in the solution can be continuously adsorbed onto the MWCNT electrode and react with $\text{S}_2\text{O}_8^{2-*}$, giving rise to an enhanced elimination performance.

3.5. Stability of AQCDI/PDS/1.2V system for acyclovir degradation

The stability is an important factor for application of PDS-based oxidative system in practical organic pollutants treatment whereas most carbocatalysts suffer from poor stability. The AQCDI/PDS/1.2V system was tested for 11 cycles and the acyclovir degradation efficiencies are shown in Fig. 5. It was demonstrated that the degradation efficiency only decreased slightly (less than 5%) after 11 cycles, implying a good reusability of AQCDI/PDS/1.2V system for catalytic oxidation. The AQCDI/PDS/-1.2V system was also tested for 3 cycles and the acyclovir degradation efficiencies are shown in Fig. S6. Clearly, the degradation efficiency barely decreased in the 3 cycles. Compared to the MWCNTs/PDS system, the better stability



Scheme 1. Proposed mechanism of removal of organic pollutant by AQCDI/PDS/1.2V system. R represents the organic molecule and X represents the active sites in MWCNTs.

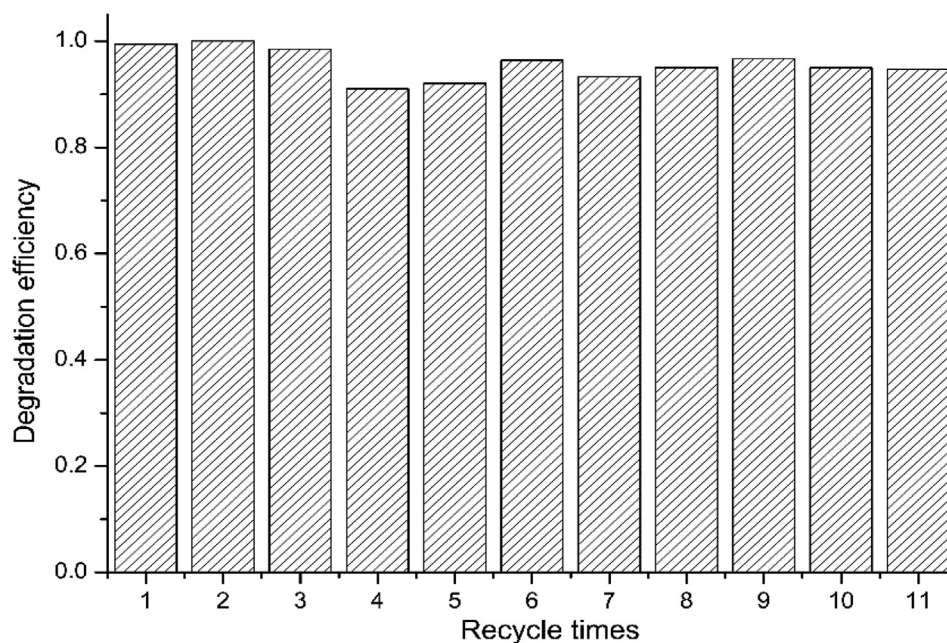


Fig. 5. Acyclovir degradation by AQCDI/PDS/1.2V system in consecutive tests. Conditions: $[\text{Acyclovir}]_0 = 0.45 \text{ mM}$; $[\text{PDS}]_0 = 11.1 \text{ mM}$. Every cycle represents 120 min of degradation process.

of polarized MWCNTs-catalyzed PDS activation system may be attributed to the reasons that the continuous charges on the surface of MWCNTs which serve as persulfate activators reduce the loss of active sites in MWCNTs and the polarization of MWCNT electrodes probably prevent the coverage of certain kinds of intermediates on the surface of MWCNTs. More cycles will be conducted in future studies to evaluate the long-term operation of AQCDI/PDS/1.2V system.

3.6. Energy consumption of AQCDI/PDS system for organic pollutants removal

To promote the practical application of polarized MWCNT-

catalyzed PDS activation with an AQCDI unit cell for organic pollutants abatement, energy consumption is an important economical index to be taken into account. In this work, the TOC removal efficiency and specific energy consumption per unit TOC mass removed (EC_{TOC} , Text S6) (Dominguez et al., 2018) of different organic pollutants were evaluated for AQCDI/PDS/1.2V and AQCDI/PDS/-1.2V systems (Table 2). It can be seen that higher mineralization rate and lower EC_{TOC} were achieved by AQCDI/PDS/1.2V system. Compared to the electro-oxidation process and electro-Fenton process (the derived EC_{TOC} is usually more than $0.1 \text{ kWh (gTOC)}^{-1}$) (Dominguez et al., 2018; Sirés et al., 2014), the calculated EC_{TOC} in this work were much lower, demonstrating that polarized MWCNTs-catalyzed PDS activation is an energy-

Table 2
TOC removal and specific energy consumption per unit TOC mass removed (EC_{TOC}) for organic pollutants removal by AQCDI/PDS systems.

Pollutants	TOC removal (%)		EC_{TOC} (kWh (gTOC) $^{-1}$)	
	AQCDI/PDS/1.2V	AQCDI/PDS/-1.2V	AQCDI/PDS/1.2V	AQCDI/PDS/-1.2V
Acyclovir	24.5	23.2	1.3×10^{-2}	6.0×10^{-2}
Phenol	67.4	14.9	4.7×10^{-3}	8.9×10^{-2}

efficient approach for wastewater remediation. Nevertheless, both acyclovir and phenol could be almost completely degraded by AQCDI/PDS/1.2V system, a much higher EC_{TOC} was achieved for acyclovir removal. This is because the intermediates during acyclovir degradation were more persistent and more difficult to be mineralized (Li et al., 2016), as evidenced by the lower TOC removal. Based on the above results, it is proposed that our AQCDI/PDS/1.2V system may serve as an alternative to other electrochemical oxidative systems for abatement of organic pollutants which can be easily mineralized like phenol in real wastewater in terms of energy consumption.

3.7. Influence of pH on acyclovir degradation by AQCDI/PDS/1.2V system

To explore the adaptable pH ranges of AQCDI/PDS/1.2V system, the oxidation was performed at different initial pH of 2, 4, 6, 8, 10. As displayed in Fig. 6a, the pH values present marginal impact on catalytic degradation, suggesting that AQCDI/PDS/1.2V system can maintain the high oxidative efficiency within a wide pH range.

3.8. Influence of voltage on acyclovir degradation by AQCDI/PDS system

During the electrosorption process, the voltage is a critical factor controlling the electrosorption capacity of peroxide ions and organic compounds. The rising voltage can lead to a stronger electrostatic attraction of ions and organics to the electrode, giving rise to a faster PDS activation and higher degradation efficiency. As expected, acyclovir degradation was accelerated when the voltage was increased from 0.4 V to 1.2 V (Fig. 6b). However, further increase of voltage leads to the declined degradation of acyclovir, probably due to the occurrence of redox reaction on the MWCNT anode resulting from the water hydrolysis (1.23 V). Therefore, 1.2 V is the optimal voltage for AQCDI/PDS system in this work.

3.9. Influence of PDS concentration on acyclovir degradation by AQCDI/PDS/1.2V system

Different loadings of PDS were added into the acyclovir solution in the AQCDI/PDS/1.2V system as shown in Fig. 6c. Clearly, the acyclovir degradation was accelerated with the increase of PDS concentration during the electro-activation. The mass transport of PDS towards the electrode surface was facilitated at higher PDS concentrations, which is beneficial to the electro-activation process and acyclovir degradation.

3.10. Influence of presence of inorganic ions on the degradation of acyclovir by AQCDI/PDS/1.2V system

Salts and diverse natural organic matters are ubiquitous in the industrial and domestic wastewater. It has been reported that chloride ions Cl^- , HCO_3^- , and CO_3^{2-} ions can affect the degradation of organic pollutants in radical-based AOPs because of the non-selective nature (Anipsitakis et al., 2006; Bennedsen et al., 2012; Yang et al., 2014). However, the influence of inorganic ions on the nonradical oxidation from MWCNT anode-catalyzed PDS activation is still unclear. Therefore, the influence of anions with different valences including Cl^- , CO_3^{2-} , and PO_4^{3-} on acyclovir degradation by AQCDI/PDS/1.2V system was investigated in this work.

In $SO_4^{\bullet-}$ -based AOPs systems, Cl^- can be oxidized into chlorine radicals by $SO_4^{\bullet-}$. The chlorine radicals may enhance or inhibit the degradation of organic pollutants which is dependent on the properties of the target organic compounds (Yang et al., 2014). For nonradical oxidation process, several studies have demonstrated that the degradation of organic pollutants could hardly be affected by the presence of Cl^- probably due to the low reactivity of generated ROS for Cl^- (Duan et al., 2018b; Lee et al., 2015; Zhu et al., 2018). In this study, Fig. 7a manifested that addition of 11.1 mM NaCl barely inhibited the acyclovir degradation by AQCDI/PDS/1.2V system. The degradation rate was somehow depressed at the beginning but the acyclovir could still be completely removed within 120 min when 22.2 mM NaCl was added, probably because the two Cl^- anions competed with one $S_2O_8^{2-}$ anions to be electrochemically adsorbed onto the surface of MWCNT anode. With the further increase of NaCl concentration, PDS may be partially activated by NaCl (Chen et al., 2016; Yuan et al., 2011), resulting in a slightly improved degradation of acyclovir. Overall, the above results also confirmed that nonradical oxidation pathway plays the dominated role in MWCNT anode-catalyzed PDS activation.

Carbonate is an important scavenger of free radicals to generate $CO_3^{\bullet-}$ which has a lower reactivity with respect to $SO_4^{\bullet-}$ and $HO^{\bullet}$ (Bennedsen et al., 2012). Therefore, the effect of CO_3^{2-} on the degradation of acyclovir was investigated. Fig. 7b shows that the addition of 11.1 mM CO_3^{2-} slightly inhibited the degradation of acyclovir, which possibly resulted from the competitive electrosorption between CO_3^{2-} and $S_2O_8^{2-}$ onto the MWCNT electrode, both of which are negatively charged with the same valence. The rapid decrease of acyclovir concentration at the beginning of the degradation process is probably because that CO_3^{2-} may also decompose PDS to produce reactive species for acyclovir oxidation (Jiang et al., 2017). The fact that activation efficiency of PDS is related to the electrosorption capacity of the $S_2O_8^{2-}$ ions was further verified when PO_4^{3-} ions were present in the AQCDI/PDS/1.2V system.

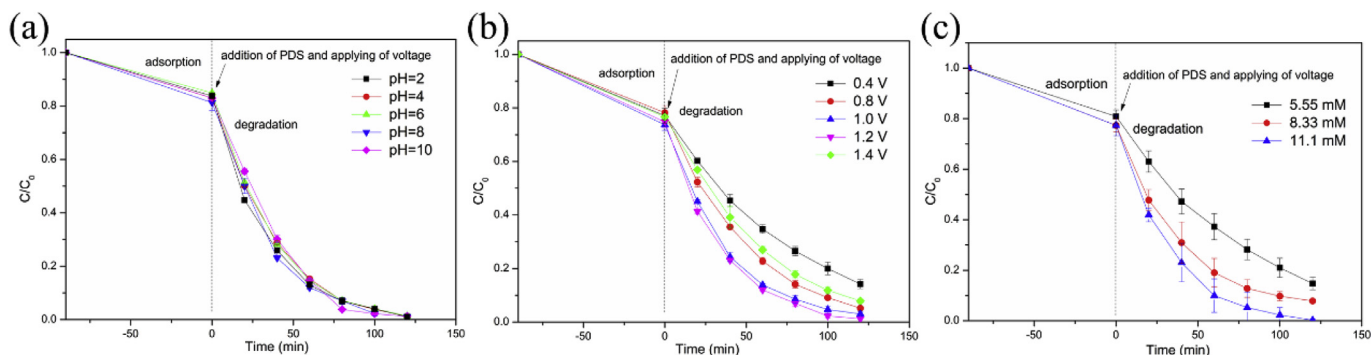


Fig. 6. Impact of (a) pH on acyclovir degradation by AQCDI/PDS/1.2V system, conditions: $[Acyclovir]_0 = 0.45$ mM; $[PDS]_0 = 11.1$ mM; (b) voltage on acyclovir degradation by AQCDI/PDS system, conditions: $[Acyclovir]_0 = 0.45$ mM; $[PDS]_0 = 11.1$ mM; (c) PDS concentration on acyclovir degradation with AQCDI/PDS/1.2V system, conditions: $[Acyclovir]_0 = 0.45$ mM.

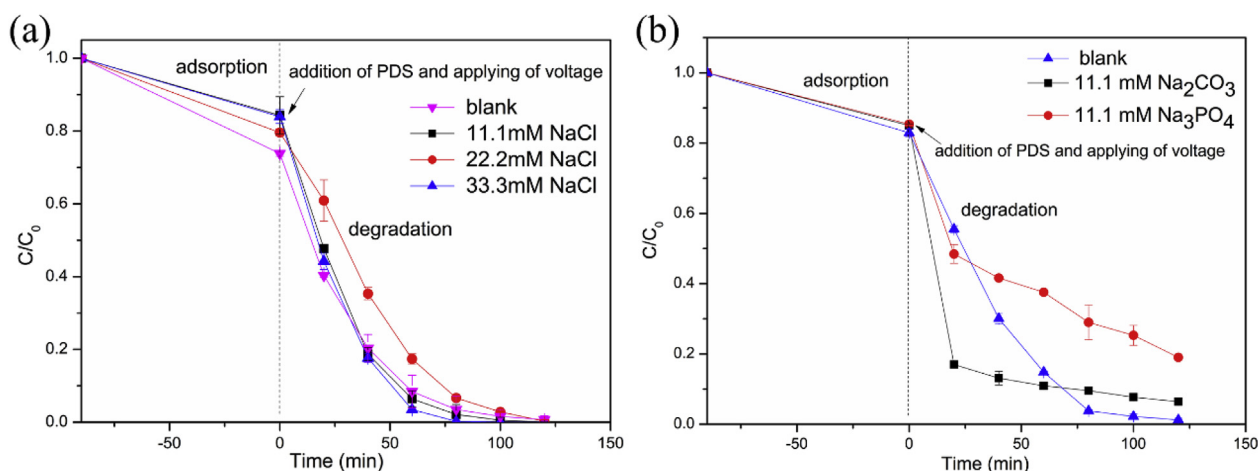


Fig. 7. Impact of water matrix (a) Cl^- and (b) CO_3^{2-} or PO_4^{3-} on acyclovir degradation with AQCDI/PDS/1.2V system. Conditions: $[\text{Acyclovir}]_0 = 0.45 \text{ mM}$; $[\text{PDS}]_0 = 11.1 \text{ mM}$.

Clearly, a significant inhibitory effect on the acyclovir degradation was observed when $11.1 \text{ mM PO}_4^{3-}$ was added. It has been reported that the normalized capacity of activated carbon electrodes for various anions increased with the ionic strength of the anions (Chen et al., 2015). Thereby, electrosorption of $\text{S}_2\text{O}_8^{2-}$ onto MWCNT anode were suppressed when PO_4^{3-} and $\text{S}_2\text{O}_8^{2-}$ ions were both present in the solution, giving rise to a declined PDS activation and acyclovir degradation.

4. Conclusions

In summary, enhanced elimination of organic contaminants in aqueous solution by polarized MWCNTs-catalyzed PDS activation using an AQCDI unit cell than MWCNTs/PDS system was demonstrated. Compared with MWCNT cathode, activation of PDS at MWCNT anode attained higher degradation efficiency due to the electrostatic attraction between $\text{S}_2\text{O}_8^{2-}$ anions and anode. Surface-bounded activated PDS was revealed to be the primary ROS involved in the nonradical oxidation pathway induced from both MWCNTs/PDS and AQCDI/PDS oxidative systems, but the structures, electronic states and oxidative capacity of activated PDS in these systems were different. DFT calculations suggested that positive polarization of MWCNT electrode further enlarged the S–O bond of surface adsorbed $\text{S}_2\text{O}_8^{2-}$ and improved its oxidative capacity remarkably, whereas negative polarization of MWCNT electrode resulted in a larger stretch of O–O bond and a little increase of oxidative capacity of the adsorbed activated $\text{S}_2\text{O}_8^{2-}$. In addition, AQCDI/PDS/1.2V system was found to be more stable than the MWCNTs/PDS system for acyclovir degradation. The optimized conditions for AQCDI/PDS system to remove acyclovir was respectively 1.2 V and 11.1 mM PDS, and the optimized system could be adapted to a wide pH range (2–10). EC_{TOC} as the economic factor was calculated for AQCDI/PDS/1.2V system and a low cost of energy was demonstrated for this system. The presence of high concentration of Cl^- could hardly impede the acyclovir degradation, while presence of CO_3^{2-} or PO_4^{3-} inhibited the degradation due to the competitive adsorption between $\text{S}_2\text{O}_8^{2-}$ with CO_3^{2-} or PO_4^{3-} . Using positively polarized MWCNT electrode for PDS activation may serve as an energy-saving and efficient technology for practical remediation of aqueous organic pollutants.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.watres.2019.115043>.

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