Degradation of aniline by electrochemical activation of peroxydisulfate at MWCNT cathode: The proofed concept of nonradical oxidation process

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HIGHLIGHTS

- Peroxydisulfate (PDS) was activated under a low working voltage by using a multi-walled carbon nanotube (MWCNT) cathode.
- Nonradical oxidation pathway was proposed to be induced from the electrochemical activation (EC) of PDS at MWCNT cathode.
- Enhanced degradation of aniline with lower energy consumption was achieved by EC/MWCNTs/PDS system.

ARTICLE INFO

ABSTRACT

Enhanced elimination of aniline in aqueous solution was achieved by coupling electrosorption of aniline and electrochemical activation of peroxydisulfate (PDS) at multi-walled carbon nanotube (MWCNT) cathode, in which a synergistic effect occurred. It was found that PDS could be effectively activated under a small voltage at MWCNT cathode owing to the specific pore structures of MWCNTs. A nonradical oxidation pathway instead of radical-based oxidation was proposed from the cathodic activation of PDS, wherein PDS molecules with a modified electronic structure was suggested to be the principal reactive species. Meanwhile, the influences of various operation parameters such as electrode potential, PDS concentration, presence of chloride ions on the elimination efficiency, and the stability of MWCNT electrode were also attempted. Therefore, the electrochemical activation of PDS by MWCNT cathode is a promising energy-saving method for the treatment of organic pollutants in wastewater.

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1. Introduction

Aniline with high toxicity and potential carcinogenicity to human beings has been recognized as one of the major environmental contaminants (An, 2011; Li et al., 2012) since it is commonly used as precursors for synthesis of various chemicals including isocyanate, polyurethane, dyes, pharmaceuticals, pesticides, and rubber additives (Zhang et al., 2015). Therefore, efficient approaches to remove aniline from the industry wastewater prior to the discharge into the aquatic environment are very necessary. For instance, photocatalytic degradation (Wang et al., 2015), microbial degradation (Dong et al., 2015) as well as in situ chemical oxidation (ISCO) have been reported for removing aniline.

Among the various approaches, ISCO as a simple, easy-control and highly efficient technology, has been widely applied for soil and groundwater remediation (Seol et al., 2003; Kubal et al., 2008). Peroxymonosulfate and peroxydisulfate (PDS) are new green oxidants and their applications in ISCO technology have attracted a lot of attention recently (Tsitonaki et al., 2010; Huang et al., 2013; And and Dionysiou, 2017; Luo et al., 2017). For elimination of organic pollutants, PDS needs to be activated to generate various oxidizing

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species (radical or nonradical). Activation of PDS can be achieved by different approaches including heating (Ji et al., 2015), UV irradiation (Gao et al., 2012), sonication (Wang and Zhou, 2016), microwave irradiation (Qi et al., 2014), electrochemical method (Chen and Huang, 2015b) and various catalysts (e.g. transition metals (Anipsitakis and Dionysiou, 2004), alkaline (Furman et al., 2010), carbon materials (Sun et al., 2012; Duan et al., 2015a, 2016), or even organic quinone (Fang et al., 2013)). Among these methods, electrochemical (EC) method has attracted increasing attention because it is versatile, controllable and environmental-friendly (Brillas and Casado, 2002; Govindan et al., 2014).

In electrochemical activation of PDS, different electrodes were studied. Iron plate as a sacrificial electrode has been commonly used for activating PDS to generate sulfate radicals ($SO_4^{\bullet-}$) to attack the organic compounds, while the disposal of iron sludge produced in this approach increases the cost (Luo et al., 2015; Silveira et al., 2017). Chen et al. (Chen et al., 2014; Chen and Huang, 2015c) and Ma et al. (Song et al., 2017) reported the EC activation of PDS at platinum (Pt) cathode and anode, respectively. Their results showed that $SO_4^{\bullet-}$ mainly contributed to the mineralization of organic pollutants in the cathodic activation of PDS while nonradical oxidation pathway was involved in the degradation of pollutants by anodic activation of PDS. Interestingly, incorporation of PDS activation into a photoelectrocatalytic process for Cu-EDTA decomplexation was also demonstrated, where a stainless steel mesh worked as cathode to decompose PDS into $SO_4^{\bullet-}$ (Zeng et al., 2016). Besides these metallic electrodes, boron-doped diamond (BDD) electrode working as anode for PDS activation was also reported (Farhat et al., 2015). Nonradical pathway by the PDS activation at the BDD anode was suggested to be responsible for diatrizoate degradation, without direct evidence though. In the above EC studies, high voltage or high current density was usually applied, thus increasing the energy consumption and hindering the practical application of EC activation of PDS in environment remediation.

Carbon nanotubes (CNTs) have been widely utilized as electrode materials for electrosorptive removal of salts and organic pollutants in wastewater due to the good electrical conductivity, chemical stability and large surface area of CNTs (Li et al., 2011; Nie et al., 2012). The removal of salts or organic pollutants by electrosorption is realized by imposing an external electrical field (usually the voltage applied is no more than 1.2 V) onto the electrodes immersed in an aqueous solution and the polarized electrodes thus attracting the oppositely charged species onto their surfaces, which is a non-Faradic process (Foo and Hameed, 2009). Therefore, it is deduced that CNTs as cathode for EC activation of PDS can enhance the removal efficiency of organic pollutants. On the one hand, the pollutants can be partially removed by the electrosorption process. Simultaneous PDS activation and electrosorption on the surface of porous carbon electrode can facilitate the electron transport between the generated reactive species and the target pollutants, which is beneficial for the degradation of pollutants. However, the EC activation of PDS at multi-walled CNT (MWCNT) cathode have been rarely reported in the literature. Additionally, though the EC activation of PDS as aforementioned showed $SO_4^{\bullet-}$ generation from the cathodic activation by metal electrodes, mechanism involved in the EC activation of PDS at MWCNT cathode is not clear because much lower working voltage compared to previous studies (Chen and Huang, 2015a, 2015c; Song et al., 2017) may result in the formation of different reactive species.

In this work, MWCNT electrode was prepared and used as the cathode for EC activation of PDS for the degradation of aniline. The operational conditions were optimized in order to achieve high removal efficiency of the target organic. Radical scavenging experiments were performed to identify the primary oxidizing

species produced in the electro-activation of PDS process. Finally, the stability of such an EC/MWCNT/PDS system for aniline degradation was evaluated.

2. Materials and methods

2.1. Materials

MWCNTs with a purity >97%, outer diameter of 7—15 nm and length >5 μm were purchased from Shenzhen Nanotech Port Co. Ltd. The samples were heated in air at 500 °C for 30 min in order to remove the amorphous impurities. N2 adsorption—desorption isotherms and pore size distribution of pristine MWCNTs and treated MWCNTs were illustrated in Fig. SM-1. Graphite sheets with a thickness of 0.5 mm were obtained from Beite Graphite Company (Yichang, China). Aniline monomer (ACS, $\geq$ 99.0%), polyvinyl alcohol (PVA), acyclovir and glutaric acid were purchased from Aladdin (Shanghai, China). Sodium peroxydisulfate (ACS, $\geq$ 99.0%) was provided by Acros Organics. Methanol of chromatographic grade was supplied by ANPEL Laboratory Technologies (Shanghai) Inc. Other chemicals of analytical grade were purchased from Damao Chemical Reagent Factory (Tianjin, China). All solutions were prepared using ultrapure water of 18.25 mΩ cm.

2.2. Electrochemical experiments

MWCNT electrode was fabricated by a casting method using PVA as a binder. In brief, 85 mg MWCNTs and 15 mg PVA were dispersed into water and the suspension was stirred at 80 °C for 4 h in order to obtain a homogenous slurry. Then the slurry was casted onto a graphite sheet (4.5 cm × 4.5 cm) used as a current collector, followed by drying in an oven at 100 °C for 2 h.

The electrochemical cell used in this work is mainly composed of two supporting plates made of polymethyl methacrylate, a graphite sheet as anode, the as-prepared MWCNT cathode and a piece of nylon cloth as spacer (Fig. 1). Two Pt ribbons were used as electrode leads for connecting to the power supplier. The cell was
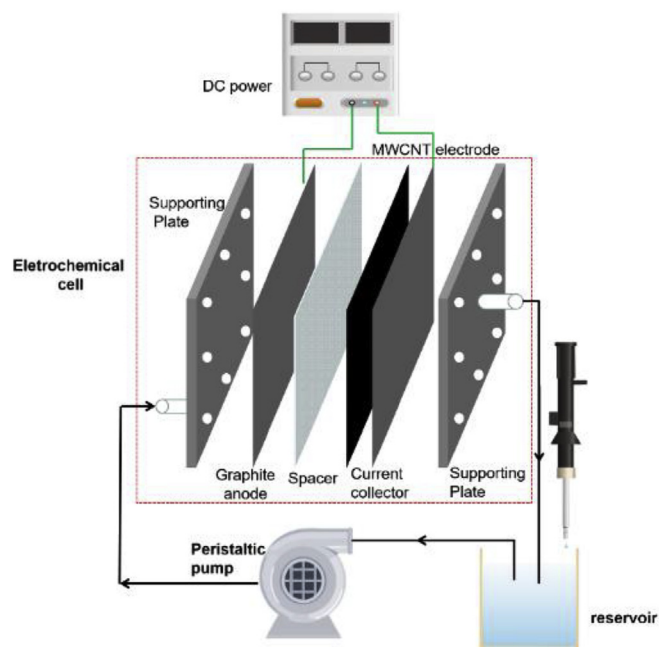

Fig. 1. Schematic diagram of electrochemical activation of PDS and aniline degradation experiment.

assembled with rubber gaskets and bolt to ensure sealing. Batch-mode experiments were performed in a continuously recycling system. In each experiment, 100 mL stock solution was continuously pumped into the cell by a peristaltic pump and the effluent returned to the EC cell. It takes less than 1 s for the stock solution to arrive at the surfaces of electrodes and takes 5 s for the stock solution to start from the reservoir and to go back to it. A CHI electrochemical workstation (CH Instruments Ins., Shanghai) was used to impose a given potential to the EC cell. One mL sample was withdrawn from the solution reservoir at predetermined time intervals and filtered through a syringe filter with polyether sulfone membrane of 0.22 μm pore size into a HPLC vial for analysis. It should be noted that, before adding PDS into the aniline solution and applying the voltage to initiate the degradation process, the solution was pumped to flow through the EC cell repeatedly for 80 min to establish the adsorption-desorption equilibrium of aniline on the MWCNT electrode. The electrosorption experiment was conducted without adding PDS. The oxidation experiments with PDS alone was performed by stirring the mixed solution of PDS and aniline in a conical flask. All the experiments were performed in duplicates or triplicates.

2.3. Analytical methods

The BET specific surface area, pore size distribution and pore volume were determined through N_2 adsorption–desorption isotherms at $-196\,^\circ$C with an Autosorb iQ station (Quantachrome instrument). The concentration of aniline was analyzed by a high-performance liquid chromatography (HPLC, Elite) equipped with a UV detector. A mixture of methanol/ultrapure water (60/40, v/v) was employed as a mobile phase at a flow rate of 1 mL/min. Total organic carbon (TOC) was measured with a Shimadzu TOC analyzer (TOC-V$_{CPH}$ E200V, Japan). KI method was used to measure the concentration of PDS (Liang et al., 2008).

3. Results and discussion

3.1. Degradation of aniline by EC/MWCNTs/PDS and comparison with other systems

The removal of aniline by EC/MWCNTs/PDS system is shown in Fig. 2a. As seen, around 30% aniline was absorbed by the MWCNT electrode, ascribing to the large surface area of MWCNTs ($442\,\mathrm{m^2\,g^{-1}}$), and a 98% removal was reached within 150 min under a voltage of -0.6 V (MWCNT electrode was connected to the negative pole of power supply), indicating the efficient EC

activation of PDS at MWCNT cathode. Meanwhile, removal of acyclovir by EC/MWCNTs/PDS system was also investigated and a removal rate of 77% was achieved (Fig. 2b). For comparison, aniline removal by PDS alone, electrosorption at MWCNT cathode (electrosorption/MWCNTs), electro PDS activation at graphite cathode (EC/Graphite/PDS system), and PDS activation at MWCNTs electrode without voltage applied (MWCNTs/PDS system) were also investigated and corresponding results are shown in Fig. 2a.

It was apparent that PDS alone had low oxidative capacity towards acyclovir and aniline with around 20% degradation and graphite electrode possessed a very low adsorption capacity for aniline. The dramatic drop of aniline concentration once the voltage was applied in the EC/Graphite/PDS system should be resulted from the deposition of polyaniline film at graphite anode. In this work, the graphite paper electrode was used as both counter electrode and reference electrode for the EC activation of PDS while the electrochemical polymerization of aniline can be initialized even at a potential of 0.2 V *vs* SCE (Wei et al., 1989). As a result, formation of polyaniline at graphite anode was induced with a voltage of -0.6 V applying on the EC cell. The above result based on the EC/Graphite/PDS system also implied that electrochemical polymerization of aniline at graphite anode might contribute to the high removal rate (98%) achieved by EC/MWCNTs/PDS system as well. However, the concentration of aniline barely changed after the polymerization process in the EC/Graphite/PDS system, revealing the inability for PDS activation by such a system. The extremely low removal rate of acyclovir (<6%) as shown in Fig. 2b further demonstrated the inability for PDS activation by EC/Graphite/PDS system.

An improved PDS activation efficiency under a small voltage was exhibited by the EC/MWCNTs/PDS system, attributing to the high adsorption capacity of MWCNTs for PDS. Evidently, graphite cathode can hardly adsorb $S_2O_8^{2-}$ co-ions (ions with negative charge as MWCNT cathode) in the electrical double layers formed on the surface of the electrode because of the repulsion force and the low specific surface area of graphite electrode ($19.4\,\mathrm{m^2\,g^{-1}}$). While in the EC/MWCNTs/PDS system, a significant amount of $S_2O_8^{2-}$ anions can still be captured in the electrical double layers of MWCNT cathode at a small external current. The abundant macropores and micropores of MWCNTs are responsible for the formation of electrical double layer structure (Suss et al., 2015). The good contact between $S_2O_8^{2-}$ ions and MWCNT cathode facilitates the electron transfer at the interfaces, resulting in an enhanced PDS activation efficiency.

In the electrosorption/MWCNTs system, aniline molecules could be further removed after the adsorption-desorption equilibrium at a small negative voltage, which was in agreement with previous
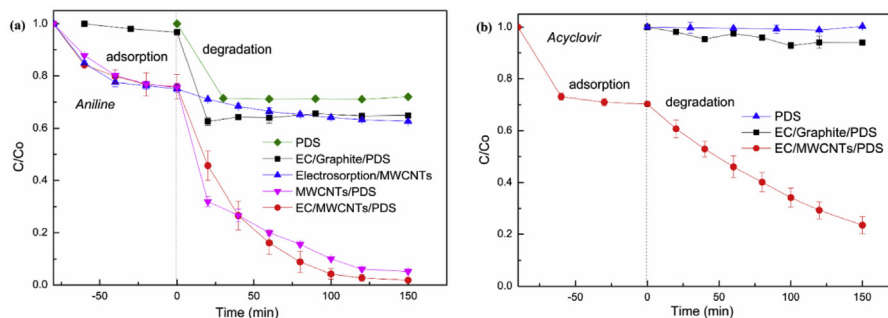

Fig. 2. (a) Concentration variations of aniline under different conditions: 5.55 mM PDS alone ◆; addition of 5.55 mM PDS and a graphite paper was used as cathode with -0.6 V voltage applied ■; applying -0.6 V onto the MWNT cathode without addition of PDS ▲; addition of 5.55 mM PDS without voltage applied to the MWCNT cathode ▼; addition of 5.55 mM PDS with -0.6 V voltage applied to the MWCNT cathode ●. Conditions: [aniline]$_0$ = 0.45 mM. (b) Concentration variations of acyclovir under different conditions: 5.55 mM PDS alone ▲; addition of 5.55 mM PDS and a graphite paper was used as cathode with -0.6 V voltage applied ■; addition of 5.55 mM PDS with -0.6 V voltage applied to the MWCNT cathode ●. Conditions: [acyclovir]$_0$ = 0.45 mM.

studies (Han et al., 2006, 2007). The electrosorption of aniline on the MWCNT cathode may be beneficial to the degradation of aniline in the EC/MWCNTs/PDS system. Simultaneous PDS activation and electrosorption of organic compounds on the surface of MWCNT electrode can facilitate the electron transport from the organic compounds to the surface confined reactive PDS complexes.

Regarding the MWCNTs/PDS system, MWCNTs have been demonstrated to be an efficient PDS activator (Sun et al., 2014; Lee et al., 2015) and the aniline removal (95%) achieved in the first cycle was similar to that of EC/MWCNTs/PDS system. However, it decreased rapidly in the second (67%) and third cycles (63%). Such observations have been reported in other carbonaceous materials-catalyzed PDS systems (Sun et al., 2012; Duan et al., 2015a; Lee et al., 2016), possibly arising from adsorption of the intermediates on the surfaces of catalysts and the coverage or oxidation of the active sites during the degradation processes. In contrast to the MWCNTs/PDS system, the aniline removal rate of EC/MWCNTs/PDS system decreased by 9% after nine cycles, suggesting that a different mechanism of PDS activation was involved in this study.

3.2. Mechanism of EC activation of PDS at MWCNT cathode

Previous studies have demonstrated that cathodic activation of PDS mainly generates $SO_4^{\bullet-}$ following Eq. (1) (Wang and Chu, 2011):

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{\bullet-} + SO_4^{2-} \tag{1}$$

To find out whether the similar reaction occurs in EC/MWCNTs/PDS system, radical scavenging experiment by adding methanol into aniline solution was conducted, since methanol can scavenge both $SO_4^{\bullet-}$ and $HO^\bullet$, and the results are illustrated in Fig. 3a. Surprisingly, excess methanol at a dose up to 180 times of PDS's molar concentration in solution hardly inhibited the degradation of aniline, indicating that neither $SO_4^{\bullet-}$ nor $HO^\bullet$ was responsible for the aniline degradation. Additionally, scavenging experiment using NaN_3 which serving as a scavenger for singlet oxygen (Qi et al., 2016) with acyclovir as the target organic pollutant was conducted and the results were shown in Fig. 3b. It was found that the addition of NaN_3 had negligible impact on the degradation of acyclovir, indicating that singlet oxygen was not responsible for the EC activation of PDS at MWCNT cathode, and other types of reactive species instead of singlet oxygen were generated from the EC activation of PDS. Therefore, in EC activation of PDS at MWCNT cathode the nonradical oxidation may play the dominant role in aniline degradation rather than relying on the free radicals.

The different mechanism involved in EC/MWCNTs/PDS system may be related to the properties of the electrode and the working voltage used. Similar to the graphite cathode, the traditional Pt, iron or stainless steel cathode for EC activation of PDS also possesses a low adsorption capacity of PDS. The activation via the one-electron reduction reaction (Eq. (1)) was mainly stimulated by the electrolysis at high working voltages used in those experiments (Govindan et al., 2014; Chen and Huang, 2015b; Zeng et al., 2016). In the current study, more $S_2O_8^{2-}$ anions can be confined in the surface pores of MWCNTs cathode. The small voltage for EC activation of PDS could not trigger the occurrence of Eq. (1), but leading to other changes of PDS. According to previous studies (Zhang et al., 2014; Duan et al., 2015b; Lee et al., 2015, 2016), even the outer-sphere interactions between CuO, CNTs or graphitized nanodiamonds and PDS can stimulate PDS molecule to form a reactive complex without instantly releasing sulfate radicals into the bulk solution. As a consequence, it could be speculated that the low current density at MWCNT cathode could also alter the arrangement of electron configuration of the adsorbed $S_2O_8^{2-}$ ions to produce activated and surface-bonded oxidizing species for degrading the electron-rich substances via electron-transfer.

Different from bulk $S_2O_8^{2-}$, the MWCNT-adsorbed $S_2O_8^{2-}$ with a modified electronic structure is highly reactive towards organic compounds, as evidenced in CuO/PDS (Zhang et al., 2014), CNTs/PDS (Lee et al., 2015), graphitized nanodiamond/PDS (Lee et al., 2016), dimensional-structured nanocarbons/PDS (Duan et al., 2015b) and EC/(Ti/Pt anode)/PDS systems (Song et al., 2017). It should be noted that the radical scavenging experiments with MWCNTs/PDS in this work (not shown) also implied the nonradical mechanisms. The electric current plays a key role in the EC activation of PDS process (Zhang et al., 2014; Duan et al., 2015b; Lee et al., 2015, 2016). A similar conclusion was also drawn for the EC/(Ti/Pt anode)/PDS system (Song et al., 2017). Unfortunately, suitable in situ characterization methods for investigating the modified electronic structure of PDS are lacking at present. Compared to the radical-based oxidation, nonradical oxidation exhibits better selectivity towards electron-rich organic compounds, hence minimizing the occurrence of undesired side reactions (Zhang et al., 2014).

3.3. Effect of working voltage on aniline degradation by EC/MWCNTs/PDS system

Various voltages ranging from −1.0 to −0.4 V were applied on the MWCNT electrode and the corresponding degradation performance of aniline in EC/MWCNTs/PDS system is shown in Fig. 4. When the working voltage was increased from −0.4 to −0.6 V, the degradation efficiency and TOC removal were improved slightly, indicating that a low voltage is efficient for the EC activation of PDS by MWCNT cathode. The small difference in degradation efficiency
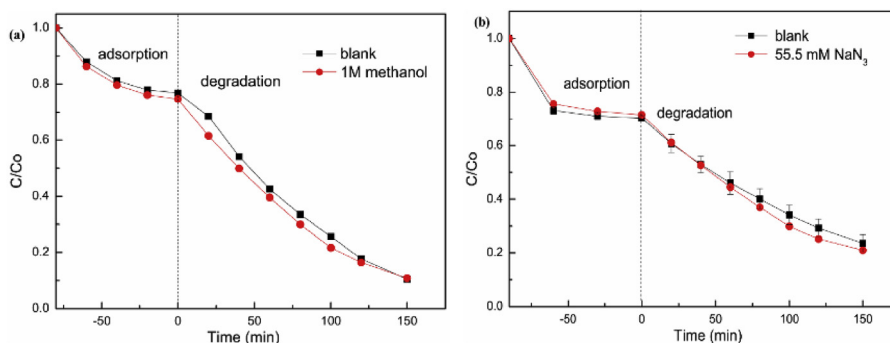

Fig. 3. Influence of the presence of (a) methanol on the degradation of aniline and (b) NaN_3 on the degradation of acyclovir: EC activation of PDS ■; EC activation of PDS with addition of 1 M methanol or 55.5 mM NaN_3 ●; Conditions: [aniline]$_0$ = 0.45 mM; [acyclovir]$_0$ = 0.45 mM; [PDS]$_0$ = 5.55 mM; voltage = −0.6 V.
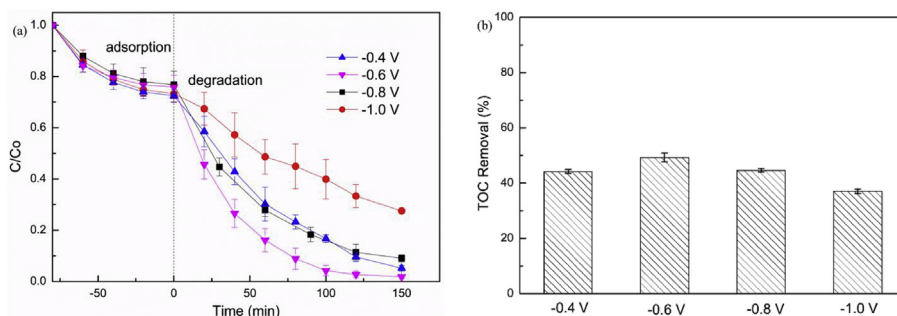
Fig. 4. Influence of voltages on aniline degradation: (a) Concentration variations of aniline and (b) TOC removal with different voltages applied to the MWCNT cathode. Conditions: $[aniline]_0 = 0.45$ mM; $[PDS]_0 = 5.55$ mM.

may be due to an increase in electrosorptive removal of aniline by MWCNT electrode in the working voltage. However, the degradation performance could not be improved at a further increasing voltage. Polymerization occurs in the aniline solution under high voltages as evidenced by HPLC chromatograms (Fig. SM-2). For raw aniline samples, a peak at retention time (t_R) of 4.7 min was observed, referring to aniline molecule. At voltage of -0.4 and -0.6 V, t_R of the aniline peak remained constant. At voltage of -0.8 and -1.0 V, the shape and t_R of the aniline peak changed gradually, suggesting polyaniline production and oxidation by activated PDS. The activated PDS exhibited a lower reactivity toward polyaniline compared to aniline, thereby resulting in a lower mineralization rate. Fig. 5c and d revealed that a higher working voltages (-1.0 V) could induce a faster polyaniline formation (at 80 min) and consequently worsen the aniline degradation.

A comparison between our EC/MWCNTs/PDS system and the EC/Pt/PDS system reported in by Chen et al. regarding the aniline degradation was made as shown in Table SM-1. It can be seen that the EC/MWCNTs/PDS system exhibited comparable TOC removal rate to the EC/Pt/PDS system but requiring much lower voltage, which can reduce the energy consumption of EC method significantly. In addition, the transient current curves during the aniline degradation process by EC/MWCNTs/PDS system were recorded (Fig. SM-3). It was clearly seen that a small hump was present in the current curves with the voltage of -0.8 V applied for EC activation of PDS, indicating the occurrence of aniline polymerization. Specific energy consumption per unit TOC mass removed (EC_{TOC}) proposed by Dominguez et al. (2018), which can be considered as an indicator of the cost of the technology when considering the practical application in wastewater treatment for aniline removal under various voltages, was also calculated in this work and listed in Table SM-2. Apparently, EC_{TOC} calculated in this work was quite low and it increased with the voltages. Meanwhile the EC_{TOC} exhibited by our EC/MWCNTs/PDS system were much lower than that (more than 1 kWh $(gTOC)^{-1}$) reported for lindane degradation by electrooxidation process with different types of electrodes (Dominguez et al., 2018), possibly due to the reasons: lindane is more difficult to be mineralized than aniline, the area of the electrodes used for lindane degradation was higher than our electrodes which could increase the resistance during the electrooxidation process, and the current density (8.33 mA cm^{-2}) was much higher than that used in our work (the average current density during the 2.5 h degradation process of aniline under a voltage of -0.6 V was estimated to be 0.12 mA cm^{-2}).

3.4. Effect of PDS concentration on aniline degradation in EC/MWCNTs/PDS system

Different amounts of PDS in the EC activation process were tested for the optimal PDS concentration for aniline degradation. It is shown in Fig. 5a that the removal rate of aniline increased slightly with the PDS concentration, implying a negligible influence of PDS dosage on the degradation efficiency. To explain such phenomena, the variation of PDS concentration during the degradation process was investigated and shown in Fig. 5b. It was found that the amount of decomposed PDS was 1.3 mM and 1.43 mM in the case of 1.85 mM PDS addition and 5.55 mM PDS addition, respectively. Such a small difference of PDS decomposition during the EC activation process with different PDS dosage suggests that the ability of our EC/MWCNTs/PDS system to activate PDS under the current conditions is limited. As a consequence, further increase of PDS concentration slightly enhances the degradation process.
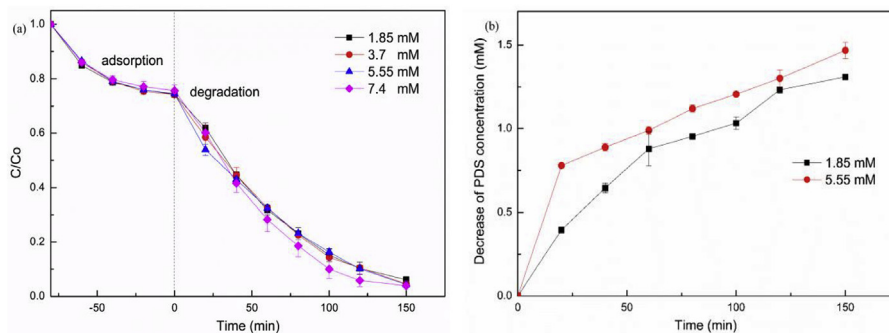

Fig. 5. Effect of initial PDS Concentration on aniline degradation: (a) Concentration variations of aniline; (b) amount variations of decomposed PDS with initial addition of PDS at 1.85 mM and 5.55 mM. Conditions: $[aniline]_0 = 0.45$ mM; voltage $= -0.6$ V.

3.5. Effect of chloride on the aniline degradation in EC/MWCNTs/PDS system

In the industrial and domestic wastewaters, salts and diverse natural organic matters are commonly present. Chloride ions, as ubiquitous aqueous ions, will influence the degradation of organic pollutants when $SO_4^{\bullet-}$-based advanced oxidation processes are involved. It has been demonstrated that chloride ions can be oxidized by $SO_4^{\bullet-}$ forming $Cl^{\bullet}$ at a high reaction rate ($k_{for} = 3.0 \times 10^8 \, M^{-1} \, s^{-1}$), and the $Cl^{\bullet}$ rapidly reacts with another chloride ion to produce $Cl_2^{\bullet-}$ (chlorine radicals), which possesses a lower redox potential ($E^0_{Cl_2^{\bullet-}/2Cl} = 2.09$ V) with respect to $SO_4^{\bullet-}$ ($E^0_{SO_4^{\bullet-}/SO_4^{2-}} = 2.5\text{-}3.1$ V) (Anipsitakis et al., 2006). The formation of chlorine radicals may inhibit or improve the organic contaminant degradation rate depending on the target contaminant (Yang et al., 2014). The effect of chloride ions on the nonradical oxidation from EC activation of PDS at MWCNT cathode were then evaluated.

Fig. 6 displays that addition of 5.55 mM Cl^- had a slight effect on aniline degradation and that the Cl^- concentrations at 11.1–16.65 mM inhibited the degradation of aniline lightly. This can be considered as another proof of nonradical mechanisms involved in the EC/MWCNTs/PDS system. The inhibitory effect of elevated Cl^- concentration in electrochemical activation of PDS process may be caused by the competitive adsorption between Cl^- and $S_2O_8^{2-}$ which are both negatively charged to be adsorbed on electrode surface (Song et al., 2017). It is interesting to mention that addition of Cl^- into carbamazepine degradation process by EC activation of PDS at Ti/Pt anode had a positive influence on the carbamazepine degradation, which was ascribed to the generation of free chlorine by electrolysis since a high current density was employed in that work (Song et al., 2017).

3.6. Stability of EC/MWCNTs/PDS system for aniline degradation

For practical application in wastewater treatment, the reusability of MWCNT electrode for EC activation of PDS and degradation of aniline is important. Recycling experiments are presented in Fig. 7. The aniline removal declined by 9% after 9 runs, which may be related to the deposition of polyaniline film on the graphite anode. With the accumulated deposition and partially oxidation of polyaniline film in each cycle, the resistance of the anode could increase to hinder the EC activation of PDS and aniline degradation.
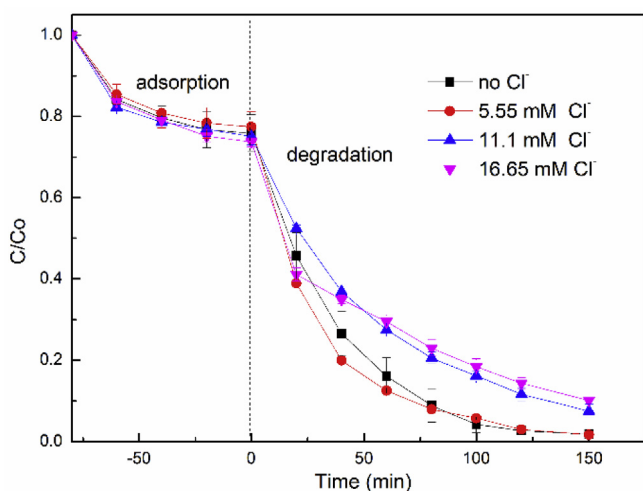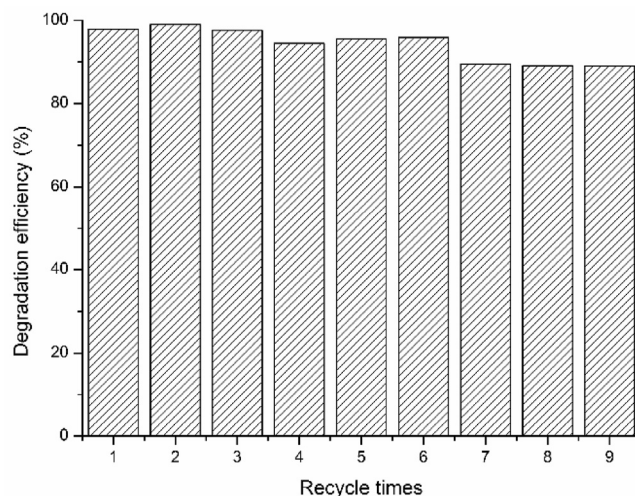

Fig. 7. Repeated aniline degradation by EC/MWCNTs/PDS system. Conditions: [Aniline]$_0$ = 0.45 mM; [PDS]$_0$ = 5.55 mM; voltage = −0.6 V. Every cycle represents 150 min of degradation process.

Meanwhile, the current evolution as a function of time during the aniline degradation process for different runs were recorded in Fig. SM-4. It was shown that the current intensity flowing through the EC/MWCNTs/PDS system decreased gradually in each run, indicating that the resistance of the whole system increased which harms the degradation performance of the system. Especially, small humps were present in the current curves during the 8th run and 9th run of aniline degradation experiments, which may be a hint of the occurrence of aniline polymerization during the degradation process. Optimization of experimental conditions to diminish the polyaniline deposition will be conducted in the future. In addition, the degradation of other organic pollutants by the EC/MWCNTs/PDS system is ongoing in our group to evaluate the potential applications in wastewater treatment of such a technique.

4. Conclusions

MWCNT electrode was used as cathode for EC activation of PDS and the degradation of aniline was investigated. A series of control experiments showed that MWCNT electrode not only enhanced the PDS activation efficiency significantly but also reduced the working voltage for efficient degradation of aniline. A synergistic effect of electrosorption of aniline and EC activation of PDS results in the facilitated electron transfer between the organic compound and generated reactive species on the surface of electrode. Nonradical oxidation process is mainly involved in the EC activation of PDS at MWCNT cathode. The formation of $S_2O_8^{2-}$ with rearranged electronic configuration was proposed to be accountable for the nonradical oxidation pathway. The presence of high concentration of Cl^- slightly impeded the aniline degradation due to the competitive adsorption between Cl^- and $S_2O_8^{2-}$. EC/MWCNTs/PDS system was stable for PDS activation and may serve as an energy-saving technology for remediation of groundwater.

Fig. 6. Influence of Cl^- on aniline degradation. Conditions: [Aniline]$_0$ = 0.45 mM; [PDS]$_0$ = 5.55 mM; voltage = −0.6 V.

talents" program of Guangdong University of Technology.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.chemosphere.2018.04.173.

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