Journal of Hazardous Materials 323 (2017) 602–610

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Effective adsorption/electrocatalytic degradation of perchlorate using Pd/Pt supported on N-doped activated carbon fiber cathode

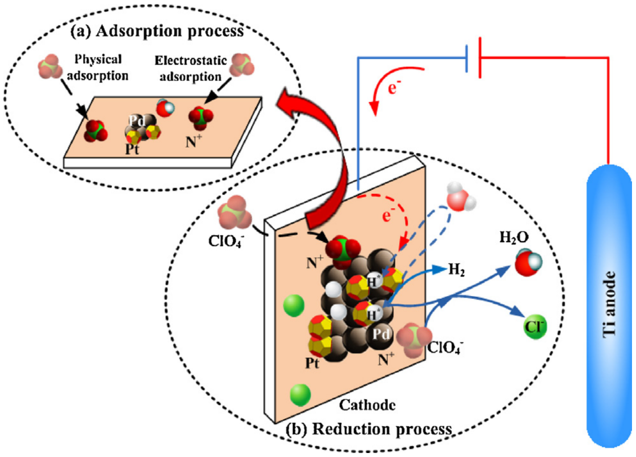
Fubing Yao[a,b], Yu Zhong[a,b], Qi Yang[a,b,*], Dongbo Wang[a,b,*], Fei Chen[a,b], Jianwei Zhao[a,b], Ting Xie[a,b], Chen Jiang[a,b], Hongxue An[a,b], Guangming Zeng[a,b], Xiaoming Li[a,b]

[a] College of Environmental Science and Engineering, Hunan University, Changsha 410082, China
[b] Key Laboratory of Environmental Biology and Pollution Control, Hunan University, Ministry of Education, Changsha 410082, China

HIGHLIGHTS

- Pd/Pt-NACF served as an adsorption/electrocatalysis electrode to reduce perchlorate.
- The possible mechanisms involved in the reaction process were explained.
- The reusability and stability of Pd/Pt-NACF bifunctional material was evaluated.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 2 May 2016
Received in revised form 15 August 2016
Accepted 21 August 2016
Available online 22 August 2016

Keywords:
Perchlorate
Adsorption
Electrocatalytic degradation
Pd/Pt-NACF electrode
Mechanism

ABSTRACT

In this work, Pd/Pt supported on N-doped activated carbon fiber (Pd/Pt-NACF) was employed as the electrode for electrocatalytic degradation of perchlorate through adsorption/electroreduction process. Perchlorate in solution was firstly adsorbed on Pd/Pt-NACF and then reduced to non-toxic chloride by the catalytic function of Pd/Pt at a constant current (20 mA). Compared with Pd/Pt-ACF, the adsorption capacity and electrocatalytic degradation efficiency of Pd/Pt-NACF for perchlorate increased 161% and 28%, respectively. Obviously, positively charged N-functional groups on NACF surface enhanced the adsorption capacity of Pd/Pt-NACF, and the dissociation of hydrogen to atomic H* by the Pd/Pt nanostructures on the cathode might drastically promote the electrocatalytic reduction of perchlorate. The role of atomic H* in the electroreduction process was identified by tertiary butanol inhibition test. Meanwhile, the perchlorate degradation performance was not substantially lower after three successive adsorption/electrocatalytic degradation experiments, demonstrating the electrochemical reusability and stability of the as-prepared electrode. These results showed that Pd/Pt-NACF was effective for electrocatalytic degradation of perchlorate and had great potential in perchlorate removal from water.

---

* Corresponding authors at: College of Environmental Science and Engineering, Hunan University, Changsha 410082, China. Fax: +86 731 88822829.
E-mail addresses: yangqi@hnu.edu.cn, yangqi0622@aliyun.com (Q. Yang), dongbowang@hnu.edu.cn (D. Wang).

http://dx.doi.org/10.1016/j.jhazmat.2016.08.052
0304-3894/

1. Introduction

Perchlorate (ClO_4^-), as a strong oxidant, is widely used in rocket propellants and explosives production [1]. Due to its high solubility in water, low adsorption to natural substance and kinetic inertness, perchlorate has been detected in ground and surface water, and soil systems, even in commercial products such as lettuce and milk [2,3]. It had been validated that high levels of perchlorate could cause adverse effects to human bodies through interfering with iodine uptake into the thyroid gland, which synthesizes thyroid hormones. For human, thyroid hormones are critical for growth, metabolism, and development of central nervous system, especially for infants and fetuses [4,5]. The U.S.EPA has established an official reference dose (RfD) of 0.7 μg/kg/day for perchlorate, which is equivalent to the Drinking Water Equivalent Level (DWEL) of 24.5 μg/L in solution.

Bioremediation and physical adsorption are most commonly used methods for perchlorate removal [6]. Previous studies had demonstrated that perchlorate could be completely reduced to chloride by enzymatic reduction functions of microorganisms in the presence of electron donor [7,8]. It seemed that biological technology was a cost-effective method for perchlorate removal, while the pathogenic micrgorganisms could also enter into drinking water during biological treatment process and bring the hazard to human beings. So it is a lower public acceptance manner for ClO_4^- removal. As regards physical adsorption, it presented as an incomplete decomposition for perchlorate removal [9]. Therefore, its major bottleneck in practical application is the disposal or regeneration of adsorbents after adsorption. Gu et al. [10] reported that the ion exchange resins saturated with perchlorate could be effectively regenerated in the concentrated $FeCl_3$—HCl solution. The desorbed perchlorate in regenerant solution was reduced to chloride by Fe(II) at above 443 K [11]. Some researchers also verified that the adsorbed perchlorate can be decomposed by thermal decomposition or radiolysis [12,13]. However, these disposal or regeneration methods are difficultly applied in practice due to their severe conditions and heavy cost.

Recently, catalytic reduction technology has been emerged and implemented as a potential alternative technology to remove the perchlorate in water [14,15]. Similar to the enzymatic reduction of perchlorate by microorganisms, perchlorate can be permanently reduced to non-toxic chloride in presence of noble metal catalysts (such as platinum [16], rhodium [15]) and reducing agents (including organic sulfide [17], hydrogen [18]). However, the catalytic reduction rate of perchlorate was extremely slow and infeasible under ambient conditions [19]. Wang et al. [20] investigated the perchlorate reduction by 78 different catalysts with H_2 as the reducing agent, but none of the catalysts showed an appreciable reaction rate at near-neutral pH. Compared with chemical catalysis, electrocatalysis has been developed in the past years due to its simple, environmentally friendly and no toxic solvents [21]. Wang et al. [22] developed an electro-dialytically assisted catalytic reduction (EDACR) system to promote the perchlorate reduction. The EDACR system incorporates the conventional electrodialysis and the electrocatalytic reaction, resulting in the rapid perchlorate reduction rate. Kim and co-workers found that 0.1 wt.% Pd supported on N-doped activated carbon (Pd/N-AC) had the adsorption/catalysis bifunction and effectively accelerated the complete decomposition of perchlorate [23]. However, to our knowledge, there are few reports on the integrated physical adsorption and electrocatalytic reduction of perchlorate in water. In present work, a Pd/Pt supported on N-doped activated carbon fiber (Pd/Pt- NACF) was served as an adsorption/electrocatalysis bifunctional electrode to remove perchlorate from water.

Herein, the main objectives of this study were (1) to investigate the adsorption capacity of Pd/Pt-NACF for perchlorate; (2) to evaluate the electrocatalytic reduction property of Pd/Pt-NACF electrode; (3) to explain the possible mechanisms involving in the adsorption/electrocatalytic reduction process; (4) to assess the reusability and stability of Pd/Pt-NACF electrode for perchlorate adsorption/electrocatalytic degradation.

2. Experimental methods

2.1. Chemical

Activated carbon fiber (ACF) was purchased from Sutong Co. Ltd. (Jiangsu, China). The experimental Ti anode was produced from a commercially pure Ti rod (HuaTai Company, China). All chemicals used were of A.R. grade and obtained from Shanghai Chemical Reagent Co. Ltd., China. Stock solutions of perchlorate and sodium sulfate were prepared by dissolving solid $NaClO_4$ and Na_2SO_4 in ultrapure water, respectively.

2.2. Preparation of cathode electrode

The ACF was pretreated with 5 M HNO_3 at 50 °C for 2 h to remove the impurities, then rinsed with deionized water until the pH value of the washing solution reached about 7, and finally dried under vacuum condition. Thermal ammonia treatment was carried out in a tube furnace. The furnace temperature was ramped at 5 °C/min to 300 °C in N_2 and maintained this temperature for 30 min. Simultaneously, N_2 was switched to pure NH_3. The temperature was heated to 700 °C, then held this temperature for 60 min, and finally cooled to ambient temperature under pure NH_3 atmosphere. In this procedure, the N_2 and the NH_3 flow rates were set at 30 mL/min. Modified samples were thoroughly washed with deionized water until the effluent solution was neutral and dried under vacuum. These samples were labeled as NACF.

Next, Pd clusters were respectively supported on the ACF and NACF using the conventional wet impregnation method with $PdCl_2$ as the impregnating solution according to the literature [24]. The impregnated samples were thoroughly washed by deionized water, reduced by ethanol and dried under vacuum, which were labeled as Pd-ACF and Pd-NACF, respectively.

Finally, Pd-ACF and Pd-NACF was soaked in 50 mL solution containing H_2PtCl_6 and polyvinyl pyrrolidone (PVP) for 15 min. The molar ratio of Pt to PVP in solution was 1:60. Then 50 mL ethanol was added into this solution and refluxed for 3 h to support the Pt on the samples. The samples were collected, thoroughly washed with deionized water and dried under vacuum, which were marked as Pd/Pt-ACF and Pd/Pt-NACF, respectively.

2.3. Adsorption of perchlorate

The perchlorate adsorption properties of ACF, Pd/Pt-ACF, NACF, Pd/Pt-NACF were studied in a batch adsorption experiments. Two types of 10 mg/L perchlorate solution, pure solution and mixed solution were used in this study. The pure solution and mixed solution was prepared by diluting the stock solutions of perchlorate using deionized water and 5 mM Na_2SO_4 solution, respectively, in which the goal of mixed solution was to investigate the perchlorate adsorption and reduction in enhanced electrical conductivity condition [25]. To avoid extremely slow adsorption kinetics of perchlorate led by the direct use of dried samples, the dried samples were immersed in deionized water for 24 h at room temperature prior to adsorption experiments.

In the kinetic study of perchlorate adsorption, 0.05 g ACF, 0.02 g NACF, 0.05 g Pd/Pt-ACF, and 0.02 g Pd/Pt-NACF samples were added to 20 mL of pure and mixed solutions. The initial pH was adjusted to 5.0 using 0.1 M H_2SO_4 or 0.1 M NaOH. The adsorption experiments were carried out at magnetic stirring 400 rpm until the adsorption

Table 1
Physical characteristics of ACF, NACF, Pd/Pt-ACF, and Pd/Pt-NACF.

Samples	BET surface area (m^2/g)	Micropore volume (cm^3/g)	Surface area of pores (m^2/g)
ACF	1359.3513	0.6119	75.330
NACF	1516.9940	0.7252	137.196
Pd/Pt-ACF	1164.7541	0.5376	71.143
Pd/Pt-NACF	1375.5692	0.6248	128.683

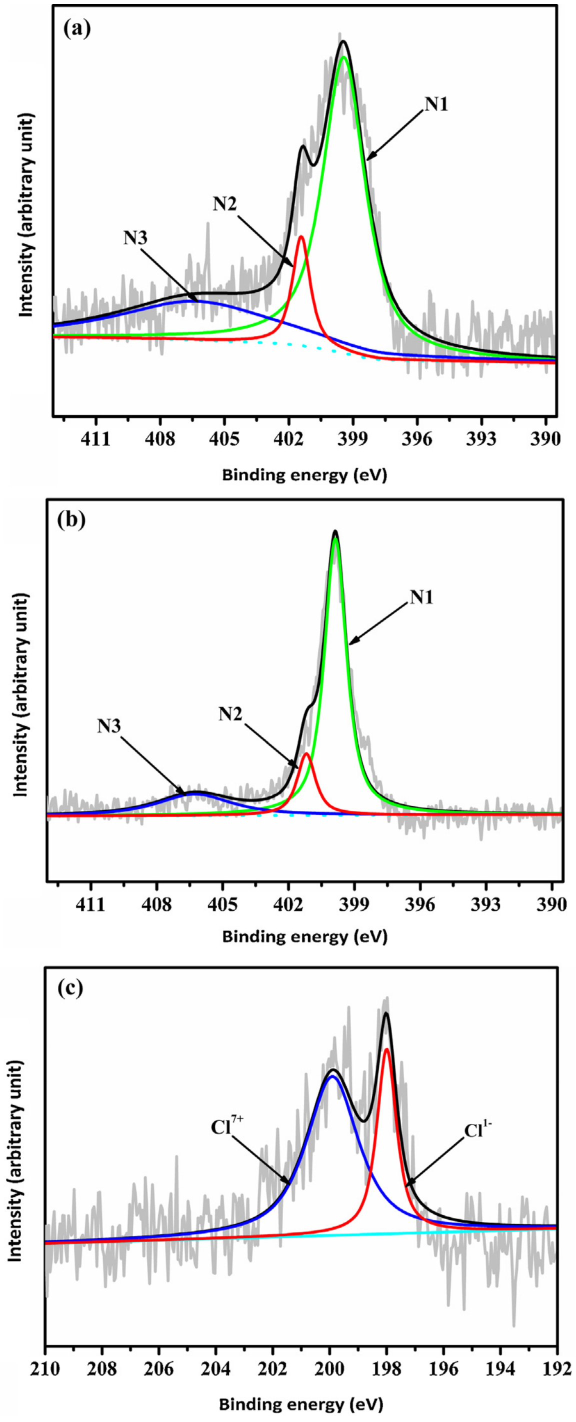


Fig. 1. N 1 s XPS spectra of NACF (a) and Pd/Pt-NACF (b), and Cl (2p) XPS spectra of Pd/Pt-NACF after reaction (c).

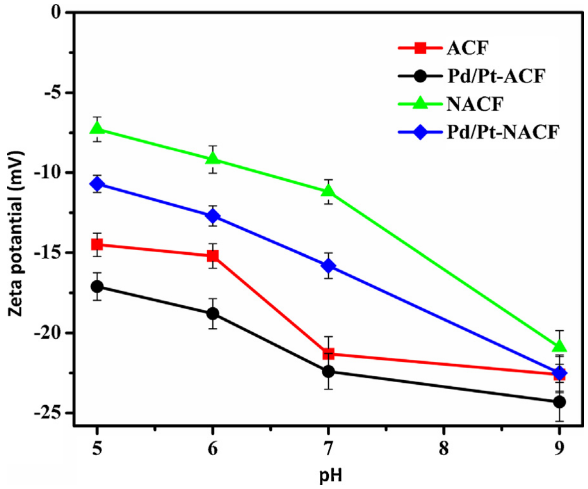


Fig. 2. Zeta potential of ACF, NACF, Pd/Pt-ACF, and Pd/Pt-NACF according to zeta potential analysis.

equilibrium. At predetermined time intervals (1, 3, 5, 10, 20, 40, 60, and 120 min), samples were taken for perchlorate analysis and the adsorption kinetics was determined. The adsorption isotherm was studied with initial perchlorate concentration varying between 2 and 20 mg L^{-1} at ambient temperature for 12 h.

The amount of adsorbed perchlorate, q (mg/g), at the specified time was calculated as follows equation

$$q = \frac{(C_0 - C_t)V}{m} \quad (1)$$

where C_0 is the initial concentration of perchlorate (mg/L), while C_t refers to the concentration of perchlorate after adsorption (mg/L), V is the volume of solution (mL), and m is the mass of dried adsorbent (g).

2.4. Adsorption/electrocatalytic degradation of perchlorate

The experiments of integrated adsorption/electrocatalytic degradation of perchlorate were carried out in a double-chamber electrochemical reactor with an effective volume of 300 mL. The cathode cell (200 mL) and the anode cell (100 mL) were separated by a cation-exchange membrane (Nafion117, Dupont), which was located at 10 mm distance from both electrodes. The geometric surface area of cathode was 600 mm^2 (20 mm × 30 mm) and the anode was Ti rod. Prior to the experiments, 200 mL mixed solution (pH=5.0 ± 0.2) was added in the cathode cell compartment, which was fully mixed by a magnetic stirrer. In order to keep stable pH in the cathode cell, a little diluted H_2SO_4 solution was added in the anode cell intermittently [26]. All experiments were conducted at an applied steady current of 20 mA. 3 mL of solution was taken regularly from the reactor cell for the analysis of perchlorate, chlorate, chlorite, and chloride.

2.5. Characterization of electrode

The specific surface area and pore volume distribution of samples were measured by ASAP 2020 Accelerated Surface Area and

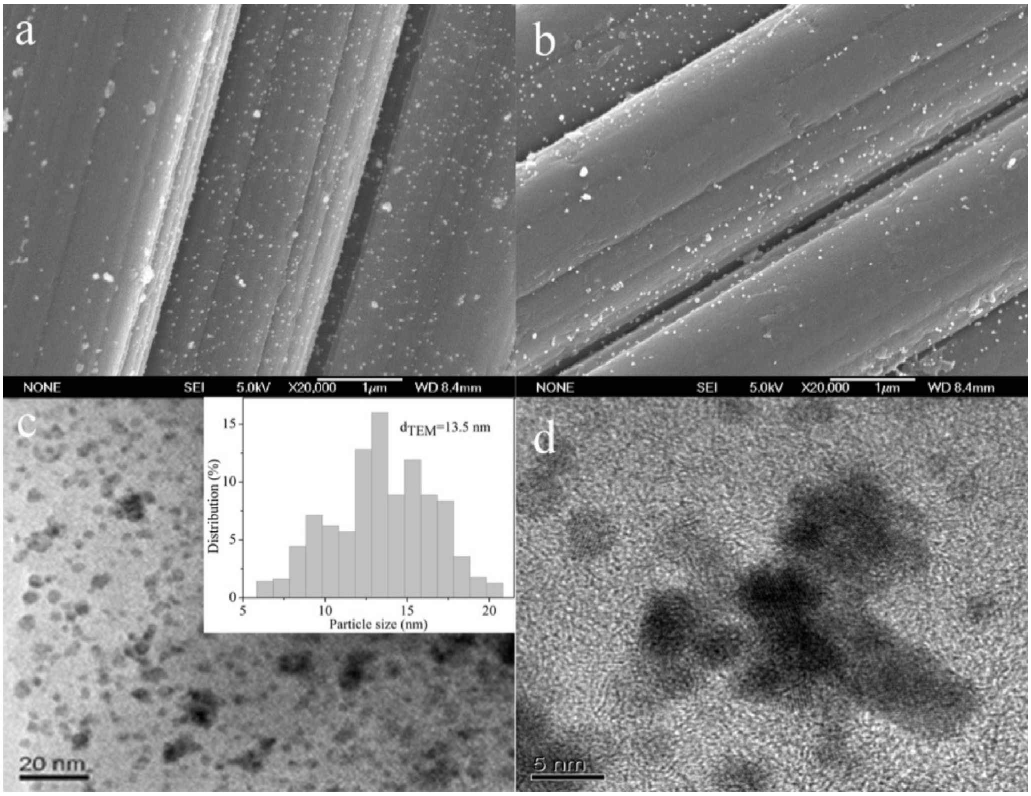


Fig. 3. SEM images of (a) Pd/Pt-ACF cathode, (b) Pd/Pt-NACF cathode, and (c, d) TEM images of Pd/Pt-NACF cathode. The inset in (c) shows a histogram of particle size distribution (d_{TEM}) for Pd/Pt-NACF cathode.

Porosimetry System (Micromeritics Instrument Corporation, USA). The X-ray photoelectron spectroscopy (XPS) was carried out in a Thermo ESCALAB 250XI spectrometer with Al Kα source. The composition of Pd/Pt was analyzed by inductively coupled plasma mass spectrometry. The surface property of all samples was examined by SEM (JSM-6700 field scanning electron microscope). X-ray powder diffraction (XRD) analysis of before and after (three cycles) the adsorption/electrocatalytic degradation experiment was carried out an X-ray powder diffractometer (Rigaka D/max 2500 v/pc X-ray) with Cu Kα radiation at 40 kV and 40 mA.

The zeta potential of all samples was determined by Zetasier Nano ZS (Malvern Instruments Ltd, UK). Firstly, 50 mL NaCl solution (0.1 M) was adjusted to different pH values between 5 and 9 by 0.1 M NaOH or HCl solution. Then 0.01 g of ACF, NACF, Pd/Pt-ACF, and Pd/Pt-NACF, ground less than 38 µm (400 mesh), were added to the solution respectively and stirred for 24 h. Approximate 2 mL of sorbent suspension was injected into the electrophoretic cell to analyze the zeta potential.

2.6. Analytical methods

The samples were centrifuged for 10 min at 5000 rpm and the supernatant was filtered with a 0.22 mm membrane filter (LC + PVDF membrane, ANPEL Laboratory Technologies Inc., Shanghai, China). The concentration of perchlorate was analyzed using Dionex ion-exchange chromatography systems (ICS-900), equipped with a 500 µL sample loop, a set of 4 × 250 mm AS16 analytical column and AG16 precolumn. The eluent (flow rate 1.0 mL/min) was set to 35 mM KOH. The intermediate and final products were measured by ion chromatography (Dionex ICS-900, USA) equipped with an IonPac AS23 analytical column and an IonPac AG23 precolumn. 9.4 mM sodium carbonate (Na_2CO_3) and 1.8 mM sodium bicarbonate ($NaHCO_3$) was used as the effluent at a flow rate of 1.0 mL/min.

2.7. Statistical analysis

All measurements were conducted in triplicate and results were expressed as mean ± standard deviation $\left(\sigma = \sqrt{\frac{\Sigma_{i=1}^{n}\left(x_i - \bar{x}\right)^2}{n-1}}\right)$.

3. Results and discussion

3.1. Electrode characterization

As shown in Table 1, NACF had greater BET surface area of 1516.9940 m^2/g and micropore volume of 0.7252 cm^3/g than ACF (1359.3513 m^2/g and 0.6119 cm^3/g). It could be explained that NH_3 was decomposed to free radicals such as NH_2, NH, and H under high temperature and these radicals attacked the carbon leading to its gasification [27]. Taken the before and after supporting Pd/Pt clusters samples into comparison, the BET surface area and micropore volume of ACF and NACF slightly decreased, indicating that the impregnation of a trace of Pd and Pt caused no significant change on the physical characteristics of ACF and NACF.

Typical XPS survey spectra of the NACF before and after supporting Pd/Pt clusters are presented in Fig. 1. The N 1 s spectrum of NACF exhibited three peaks, i.e., at 399.4 eV, 401.3 eV and 406.7 eV, which should be ascribed to pyridinic nitrogen (N1), pyrrolic nitrogen (N2), and pyridinic oxide (N3) [28]. The similar nitrogen species were also detected in Pd/Pt-NACF. The N1 (pyridinic nitrogen) was the most dominant specie for both samples (NACF and Pd/Pt-NACF). The results suggested that supporting Pd/Pt clusters did not

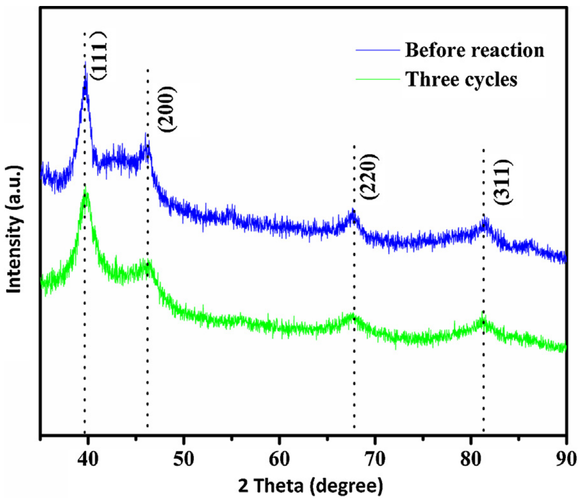


Fig. 4. XRD spectra of Pd/Pt-NACF before and after (three cycles) the adsorption/electrocatalytic degradation experiment.

substantially change the chemical nature of surface N-functional groups of NACF.

The variation of zeta potential of a particle often was used to indicate the changes of surface charge [23,29]. The zeta potential of ACF, NACF, Pd/Pt-ACF, and Pd/Pt-NACF were determined and presented in Fig. 2. The ACF and Pd/Pt-ACF displayed more negative zeta potentials than NACF and Pd/Pt-NACF over the entire experimental range of pH, which indicated that they had more negative surface charge densities. It proved the similar conclusion of previous literature that ammonia tailoring could increase the positive charge on the surface of carbon due to the incorporation of positively charged N-functional groups [29]. The zeta potentials for NACF and Pd/Pt-NACF decreased with increasing pH, suggesting that the doping N-functional groups were only weakly basic [23]. Meanwhile, Pd/Pt-ACF and Pd/Pt-NACF showed more negative zeta potentials than ACF and NACF, respectively. This revealed that supporting Pd/Pt clusters led slight decrease of the surface charge.

Elemental analysis using ICP-MS showed that 0.7 and 0.7 wt.% Pt, and 0.9 and 1.0 wt.% Pd were supported on Pd/Pt-ACF and Pd/Pt-NACF, respectively. SEM images of Pd/Pt-ACF and Pd/Pt-NACF are displayed in Fig. 3. The micrograph clearly revealed that the Pd/Pt catalytic particles uniformly distributed on the surface of Pd/Pt-ACF and Pd/Pt-NACF. The diameter distribution results (inset of Fig. 3c) showed that the average diameter of Pd/Pt clusters was about 13.5 nm (d_{TEM}). In order to achieve more quantitative information on the morphology of catalytically active Pd/Pt surfaces, the crystallinity of catalyst was also analyzed by XRD (Fig. 4). The diffraction peaks at 39.4°, 46.2°, 67.7°, and 81.1° were indexed as (111), (200), (220), and (311) planes, respectively, revealing that Pd/Pt formed unique face-centered cubic nanocrystals.

3.2. Adsorption of perchlorate

The perchlorate adsorption kinetics on ACF, NACF, Pd/Pt-ACF, and Pd/Pt-NACF were investigated in pure and mixed solutions and the results are presented in Fig. 5. Within 40 min, perchlorate adsorption reached 95% of the pseudo-equilibrium concentration. In particular, the most perchlorate adsorption taken place during the first 10 min for NACF and Pd/Pt-NACF samples. Similar phenomenon also was found in perchlorate adsorption onto Pd/N-doped activated carbon (Pd/N-AC) [23]. The fast achievement to the pseudo-equilibrium should be attributed to the small ionic radius of perchlorate (0.34 nm) and the presence of large micropore (Table 1), which provides a fast transport pathway for ClO_4^- adsorption [30].

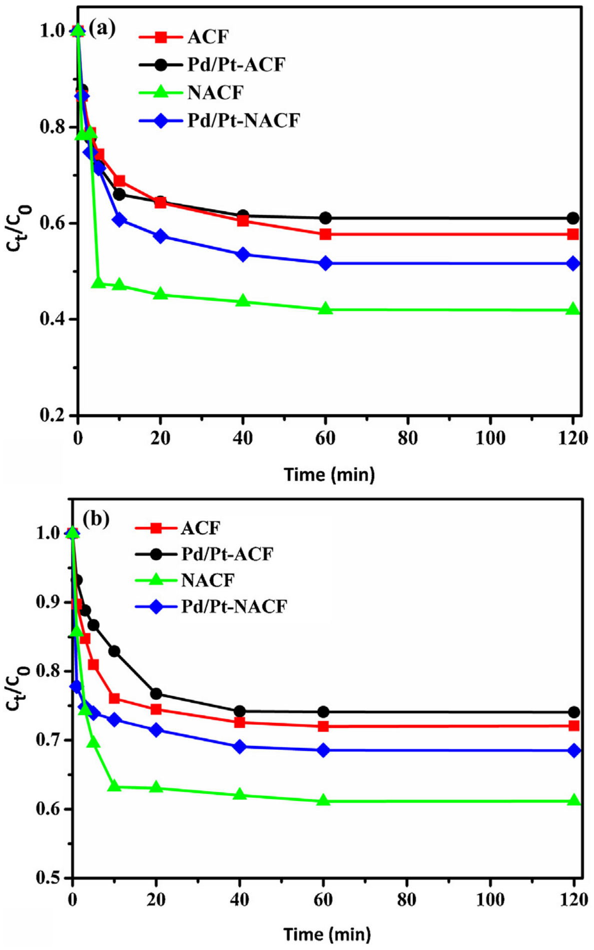


Fig. 5. Kinetics of perchlorate adsorption on ACF, NACF, Pd/Pt-ACF, and Pd/Pt-NACF in pure solution (a) and mixed solution (b).

Table 2
Langmuir isotherm parameters for perchlorate adsorption on ACF, NACF, Pd/Pt-AC, and Pd/Pt-NACF in pure and mixed solution.

Samples	q_{max}^{a}(mg/g)	K^b(L/mg)	R^2
ACF(pure)	3.65 ± 0.83	0.15 ± 0.07	0.94
NACF(pure)	7.03 ± 0.35	0.51 ± 0.10	0.98
Pd/Pt-ACF(pure)	2.44 ± 0.11	0.15 ± 0.01	0.99
Pd/Pt-NACF(pure)	5.08 ± 0.11	0.30 ± 0.02	0.99
ACF(mixed)	2.00 ± 0.29	0.15 ± 0.05	0.97
NACF(mixed)	5.50 ± 0.42	0.16 ± 0.02	0.99
Pd/Pt-ACF(mixed)	1.54 ± 0.24	0.15 ± 0.05	0.96
Pd/Pt-NACF(mixed)	4.03 ± 0.87	0.16 ± 0.07	0.95

Perchlorate adsorption isotherms on ACF, NACF, Pd/Pt-ACF, and Pd/Pt-NACF in pure and mixed solutions are displayed in Fig. 6. The classical Langmuir model (Eq. (2)) was used to fit the experimental data and the fitting results are summarized in Table 2.

$$q_e = \frac{q_{max}KC_e}{1+KC_e} \tag{2}$$

where q_e is the amount of perchlorate adsorbed (mg/g), C_e is the equilibrium concentration (mg/L), q_{max} is the maximum adsorption capacity (mg/g), and K is the Langmuir coefficient related to adsorption strength (L/mg).

According to the results in Table 2, the maximum adsorption capacities of NACF were 1.9 and 2.7 times that of ACF in pure solution and mixed solution, respectively. Compared with Pd/Pt-ACF,

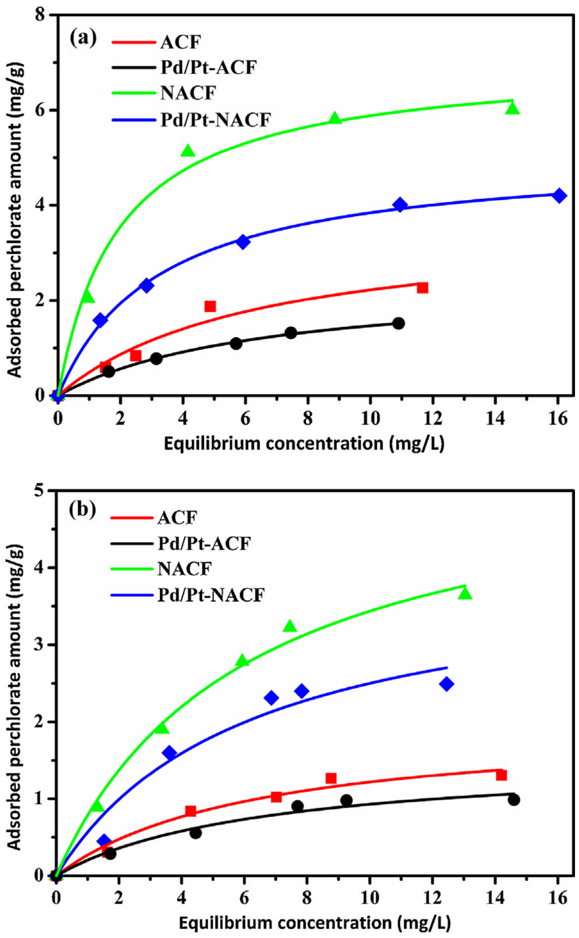


Fig. 6. Langmuir adsorption isotherms of perchlorate on ACF, NACF, Pd/Pt-ACF, and Pd/Pt-NACF in pure solution (a) and mixed solution (b).

Table 3
Correlation (R^2) between physical-chemical features listed and the maximum adsorption capacity of ACF, NACF, Pd/Pt-ACF, and Pd/Pt-NACF.

Physical-chemical features	R^2
BET surface area	0.58
Micropore volume	0.68
Average diameter	0.59
Zeta potential	0.96

the maximum adsorption capacities of Pd/Pt-NACF were 2.08 and 2.61 times in pure solution and mixed solution, respectively. These results suggested that the presence of N-functional groups could significantly enhance the perchlorate adsorption capacity. However, the K values of all samples except for ACF and Pd/Pt-ACF decreased in various degrees in mixed solutions, which indicated that adsorption of perchlorate on as-prepared samples were more easily influenced by the high concentration competing anion (sulfate).

In addition, statistical analysis indicated that there were obvious correlation between the maximum adsorption capacity (q_{max}) and zeta potential ($R^2 = 0.96$, pH = 5.0 ± 0.2) for each samples as summarized in Table 3. Chen et al. [31] found that increased perchlorate adsorption on ammonia-tailoring of GAC corresponded to increased positive surface charges with $R^2 = 0.95$. But the correlations between the maximum adsorption capacity and BET surface area, micropore volume, and average pore diameter were lower, with below 0.70 of R^2. Based on the above discussion, it could be perceived that charge-based phenomenon led to the improved adsorption capacity of NACF and Pd/Pt-NACF rather than by other physical interactions between adsorbent and adsorbate [31] and the interpretations could be supported by the XPS analysis (Fig. 1) and the zeta potential measurement (Fig. 2).

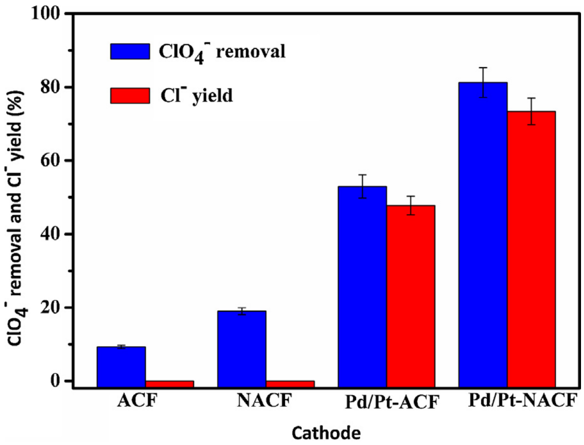


Fig. 7. Perchlorate removal and chloride yield by different cathode (Reaction conditions: initial ClO_4^- 10 mg/L, Na_2SO_4 5 mM, pH 5.0, constant current 20 mA, reaction times 8 h).

3.3. *Adsorption/electrocatalytic degradation of perchlorate*

In the present work, the electrocatalytic degradation of perchlorate with different cathodes, i.e., ACF, NACF, Pd/Pt-ACF, and Pd/Pt-NACF, was performed to investigate the role of the Pd/Pt nanostructures, the positively charged N-functional groups, and the synergistic effects of adsorption/electrocatalysis in the perchlorate degradation process.

The perchlorate removal efficiency with different cathodes is presented in Fig. 7. Among the as-prepared cathodes, Pd/Pt-NACF exhibited the highest removal efficiency for perchlorate (81%) after reaction 8 h, while it was 9%, 19% and 53% for ACF, NACF and Pd/Pt-ACF, respectively. On the one hand, the presence of Pd/Pt nanostructures could activate H_2, forming atomic H*, which is crucial for the electrocatalytic reduction perchlorate in the electrochemical removal system. On the other hand, the differences of perchlorate removal between Pd/Pt-ACF and Pd/Pt-NACF could be ascribed to the presence of positively charged N-functional groups on the surface of Pd/Pt-NACF cathode, which enhanced the adsorption sites for perchlorate adsorption. Fig. 7 showed that chloride yield was calculated to be less than 5% and 8% below the corresponding value of perchlorate removal throughout the experiments for Pd/Pt-ACF and Pd/Pt-NACF, respectively. This negligible difference revealed that perchlorate was effectively reduced to chloride. Therefore, the improved perchlorate degradation efficiency should be attributed to the synergistic effects of the enhanced adsorption led by N-functional groups and the electrocatalytic reduction induced by Pd/Pt nanostructures.

The pseudo-first-order kinetic model was used to fit the perchlorate degradation with the reaction time. The model was given by Eq. (3).

$$C_t/C_0 = \exp(-kt) \tag{3}$$

where C_t and C_0 are the perchlorate concentrations (mg/L) at times of t = t and t = 0, respectively, k is the rate constant (h^{-1}), and t is the reaction time (h). High correlation coefficient (R^2) showed that pseudo-first-order kinetic model could simulate the electrochemical perchlorate removal well (Fig. 8). The rate constant k of Pd/Pt-NACF electrode for perchlorate removal was double than that of Pd/Pt-ACF electrode.

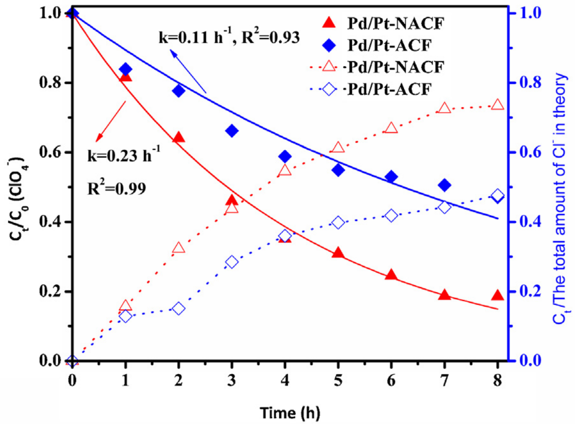


Fig. 8. Pseudo-first-order kinetic model plots for the perchlorate reduction (solid symbols represent the ClO_4^- and hollow symbols represent the Cl^-; Reaction conditions: initial ClO_4^- 10 mg/L, Na_2SO_4 5 mM, pH 5.0, constant current 20 mA, reaction times 8 h).

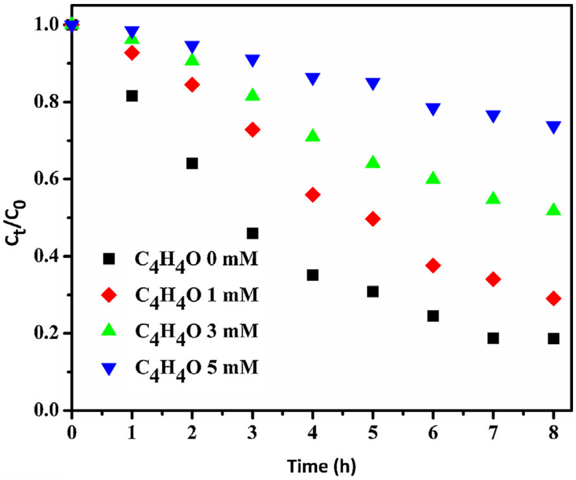


Fig. 9. Effect of $C_4H_{10}O$ concentrations on the electrocatalytic reduction of perchlorate (cathode: Pd/Pt-NACF, anode: Ti rod, initial ClO_4^- 10 mg/L, Na_2SO_4 5 mM, pH 5.0, constant current 20 mA).

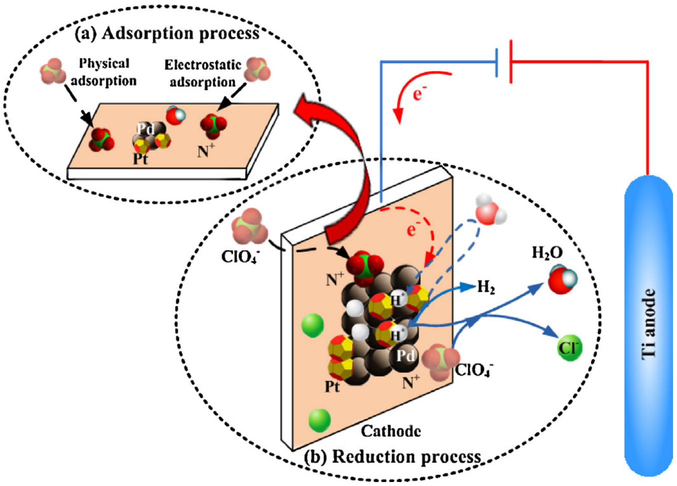
The energy consumption E (kWh/g) of perchlorate removal in this system could be calculated according to [32] .

$$E = 10^{-3} UItm^{-1} \tag{4}$$

where U is cell potential (V), I is applied current (A), t is reaction time (h), and m is mass of the removed perchlorate (mg). As listed in Table 4, the energy consumption for Pd/Pt-NACF cathode was lower than that of Pd/Pt-ACF cathode.

These results fully indicated that the double-chamber electrochemical reactor with the Pd/Pt-NACF cathode was superior to the Pd/Pt-ACF cathode for perchlorate removal due to relatively high degradation efficiency, quick reduction rate, and low energy consumption.

Previous research demonstrated that t-BuOH (tertiary butanol) could capture the atomic H^* and then converted them into relatively inert 2-methyl-2propanol radicals [33]. Hence, in order to identify the role of atomic H^* for perchlorate reduction in the electrocatalytic degradation process, batch experiments were performed with the different stoichiometric concentrations of t-BuOH. As presented in Fig. 9, the reduction of perchlorate were significantly hampered with the increasing of t-BuOH concentration, which suggested that the electrocatalytic degradation of perchlorate mainly was via the indirect reduction induced by atomic H^* in the reaction system.



Scheme 1. Schematic representation of the synergistic integration process of (a) adsorption of perchlorate on N-doped activated carbon fiber (NACF) and (b) electrocatalytic reduction of the adsorbed perchlorate to chloride by Pd/Pt supported on N-doped activated carbon fiber (Pd/Pt-NACF) electrode.

3.4. Possible mechanisms

Based on the above experimental results, the theoretical mechanism of perchlorate degradation on Pt/Pd-NACF cathode is illustrated in Scheme 1.

Firstly, the perchlorate and water molecule were adsorbed on the surface of Pd/Pt-NACF electrode. Both reactions were fast and reached the equilibrium within the shorter time (10 min).The corresponding process could be listed as followings:

$$Pd/Pt - NACF + ClO_4^- (sol) \mathit{rightarrow} Pd/Pt - NACF -ClO_4^- (ads)(Adsorption) \tag{5}$$

$$Pd/Pt - NACF + H_2O(sol) \rightarrow Pd/Pt - NACF -H_2O(ads)(Adsorption) \tag{6}$$

where sol stands for the perchlorate (water molecule) in the solution and ads refers to the adsorbed perchlorate (water molecule). The enhanced perchlorate adsorption capacity on Pd/Pt-NACF led by the presence of positively charged N-functional groups on the surface of ACF [23].

With the application of a constant current on the electrode (20 mA), the adsorbed water molecule was reduced to atomic H^* (Eq. (7)), a strong reducing agent, which could react with a series of species of oxoanion including nitrate, bromate, and perchlorate [32,34]. In addition, vigorous gas (H_2) was observed on the cathode (Eq. (8)), which could be bound and activated by the Pd/Pt nanostructures, forming atomic H^* [35,36].

$$Pd/Pt + H_2O + e^- \rightarrow Pd/Pt - H^* + OH^- (Volmerdischarge) \tag{7}$$

$$2Pd/Pt - H^* \leftrightarrow 2Pd/Pt + H_2 (Tafelreaction) \tag{8}$$

The reaction between perchlorate and H^* is a multiple step process. When direct reaction between H^* and perchlorate took place, various intermediate chloro-oxyanions and end-product chloride were produced according to the following equations.

Table 4
Comparison of energy consumption in electrocatalytic reactor with different cathodes.

Cathodes	Cell potential (V)	Applied current (mA)	Removed perchlorate (mg)	Energy consumption (kWh/g perchlorate)
Pd/Pt-ACF	11.8	20	1.0	1.8
Pd/Pt-NACF	11.2	20	1.7	1.0

$$2\mathrm{Pd/Pt-H^*} + \mathrm{ClO_4^-} \rightarrow 2\mathrm{Pd/Pt} + \mathrm{ClO_3^-} + \mathrm{H_2O}\,(\text{Hydrodeoxygenation}) \quad (9)$$

$$2\mathrm{Pd/Pt-H^*} + \mathrm{ClO_3^-} \rightarrow 2\mathrm{Pd/Pt} + \mathrm{ClO_2^-} + \mathrm{H_2O}\,(\text{Hydrodeoxygenation}) \quad (10)$$

$$4\mathrm{Pd/Pt-H^*} + \mathrm{ClO_2^-} \rightarrow 4\mathrm{Pd/Pt} + \mathrm{Cl^-} + 2\mathrm{H_2O}\,(\text{Hydrodeoxygenation}) \quad (11)$$

The step of Eq. (9) was recognized as the rate-limiting step in the electrochemical reduction perchlorate process [37]. In the integrated adsorption and electrocatalytic degradation process, if the elelctrocatalytic degradation occured only on the Pd/Pt surface, the presence of positively charged N-functional groups would not significantly affect the removal efficiency of perchlorate. According to previous literature, these results could be explained that positively charged N-functional groups not only served to increase the number of adsorption sites for perchlorate, but also might cooperate with the adsorbed water synergistically to drastically reduce the activation barrier for perchlorate reduction [23].

The balance of chlorine during the electrochemical experiment process (Fig. 8) also revealed that most of perchlorate is fully reduced. Fig. 1c showed the XPS spectra of Cl(2p) for the Pd/Pt-NACF after reaction. There were two binding energy of Cl(2p) at 197.9 eV (perchlorate) and 199.8 eV (chloride), which confirmed the presence of chlorine in the Pd/Pt-NACF. Thus, small loss of total chlorine in solution could be explained as the adsorption on the electrode surface. It is noteworthy that no other intermediate chloro-oxyanions (e.g., chlorite and chlorate) were detected in the reaction system. This suggested that the kinetic stability of chlorite and chlorate are much less than perchlorate and they would be completely reduced to chloride once formed (Eqs. (9)–(11)) [38].

3.5. Cyclic experiments

The aforementioned experiments clearly showed that Pd/Pt-NACF has obvious advantages in both adsorption and electrocatalytic degradation of perchlorate. However, whether the perchlorate adsorption/electrocatalytic degradation using Pd/Pt-NACF cathode could be repeated without loss of perchlorate degradation efficiency? To illustrate it, Pt/Pt-NACF cathode was repeatedly used three successive cycles under the identical experimental condition. After each cycle, the electrode was taken out, washed and dried for next cycle.

As depicted in Fig. 10, the perchlorate degradation efficiency was no significant decrease after three successive cycles. Moreover, the XRD patterns of Pd/Pt-NACF after three cycles showed that the used Pd/Pt-NACF maintained the similar crystal structure to the materials before adsorption/electrocatalysis experiment (Fig. 4). These results indicated that the as-prepared electrode could be re-used.

4. Conclusions

The present study demonstrated that perchlorate could be effectively electroreduced to chloride using the adsorption/electrocatalysis bifunctional material Pd/Pt-NACF as the electrode. The positively charged N-functional groups on the surface of N-doped activated carbon fiber (NACF) enhanced the surface charge and increased the active sites for perchlorate adsorption. Subsequently, the perchlorate adsorbed on Pd/Pt-NACF surface could be reduced to non-toxic chloride through the catalysis of supported Pd/Pt clusters in a double-chamber electrochemical reactor. The reduction efficiency might be governed by the atomic H* and the adsorbed perchlorate. The perchlorate removal efficiency was not obvious loss after three successive adsorption/electrocatalytic cycle experiments, suggesting its application potential in perchlorate-containing wastewater treatment.

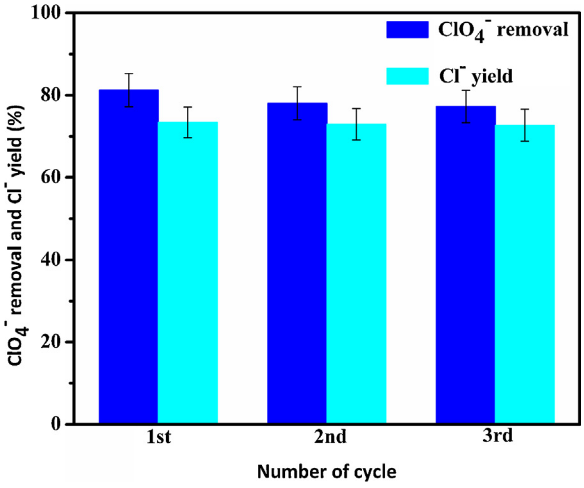


Fig. 10. Perchlorate removal efficiency during three successive adsorption/electrocatalytic degradation cycles (cathode: Pd/Pt-NACF, anode: Ti rod, initial ClO_4^- 10 mg/L, Na_2SO_4 5 mM, pH 5.0, constant current 20 mA, reaction times 8 h).

Acknowledgements

This research was financially supported by the project of National Natural Science Foundation of China (Nos. 51508178, 5147870, 51378188), Doctoral Fund of Ministry of Education of China (20130161120021) and Science and Technology Planning Project of Hunan Province, China (2015SK2067).

References

[1] P.K. Dasgupta, J.V. Dyke, A.B. Kirk, J.W. Andrew, Perchlorate in the United States. Analysis of relative source contributions to the food chain, Environ. Sci. Technol. 40 (2006) 6608–6614.
[2] B.H. John Karl, N.C. Sturchio, G. Baohua, H. Juske, G.M. Brown, J.W. Andrew, B. Jacimaria, P.B. Hatzinger, Perchlorate isotope forensics, Anal. Chem. 77 (2005) 7838–7842.
[3] A.B. Kirk, P.K. Martinelango, K. Tian, A. Dutta, E.E. Smith, P.K. Dasgupta, Perchlorate and iodide in dairy and breast milk, Environ. Sci. Technol. 39 (2005) 2011–2017.
[4] Z. Tao, W. Qian, S. Hong Wen, R. Jia, K. Kurunthachalam, Perchlorate and iodide in whole blood samples from infants children, and adults in Nanchang, China, Environ. Sci. Technol. 44 (2010) 6947–6953.
[5] S.H. Lamm, L.F. Xiao, D.M. Byrd, Perchlorate in drinking water, J. Occup. Environ. Med. 44 (2002) 393-393.
[6] B.E. Logan, Assessing the outlook for perchlorate remediation, Environ. Sci. Technol. 35 (2001) 482A–487A.
[7] B. Min, P.J. Evans, A.K. Chu, B.E. Logan, Perchlorate removal in sand and plastic media bioreactors, Water Res. 38 (2004) 47–60.

[8] J.D. Shrout, G.F. Parkin, Influence of electron donor, oxygen, and redox potential on bacterial perchlorate degradation, Water Res. 40 (2006) 1191–1199.

[9] H. Yoon, X. Meng, C. Wang, K.W. Kim, S. Bang, E. Choe, L. Lippincott, Perchlorate adsorption and desorption on activated carbon and anion exchange resin, J. Hazard. Mater. 164 (2008) 87–94.

[10] B. Gu, G.M. Brown, L. Maya, M.J. Lance, B.A. Moyer, Regeneration of perchlorate (ClO_4^-)-loaded anion exchange resins by a novel tetrachloroferrate ($FeCl_4^-$) displacement technique, Environ. Sci. Technol. 35 (2001) 3363–3368.

[11] B. Gu, W. Dong, G.M. Brown, D.R. Cole, Complete degradation of perchlorate in ferric chloride and hydrochloric acid under controlled temperature and pressure, Environ. Sci. Technol. 37 (2003) 2291–2295.

[12] E.E. Hackman, H.H. Hesser, H.C. Beachell, Detection of species resulting from condensed phase decomposition of ammonium perchlorate, J. Phys. Chem. 76 (1972) 3345–3554.

[13] D. Katakis, A.O. Allen, The Radiolysis of aqueous perchloric acid solutions, J. Phys. Chem. 68 (1964) 3107–3115.

[14] Z. Yunxia, K.D. Hurley, J.R. Shapley, Heterogeneous catalytic reduction of perchlorate in water with Re-Pd/C catalysts derived from an oxorhenium(V) molecular precursor, Inorg. Chem. 50 (2011) 1534–1543.

[15] M. Wasberg, G. Horányi, The reduction of ClO_4^- ions on Rh electrodes, J. Electroanal. Chem. 385 (1995) 63–70.

[16] M.Y. Rusanova, P. Polášková, M. Muzikař, W.R. Fawcett, Electrochemical reduction of perchlorate ions on platinum-activated nickel, Electrochim. Acta. 51 (2006) 3097–3101.

[17] L.D. Mcpherson, D. Markus, S.I. Khan, S. Thomas, M.M. Abu-Omar, Multielectron atom transfer reactions of perchlorate and other substrates catalyzed by rhenium oxazoline and thiazoline complexes: reaction kinetics, mechanisms, and density functional theory calculations, Inorg. Chem. 43 (2004) 4036–4050.

[18] R. Mahmudov, Y. Shu, S. Rykov, J. Chen, C.P. Huang, The reduction of perchlorate by hydrogenation catalysts, Appl. Catal. B: Environ. 81 (2008) 78–87.

[19] G.G. Láng, G. Horányi, Some interesting aspects of the catalytic and electrocatalytic reduction of perchlorate ions, Electroanal. Chem. 552 (2003) 197–211.

[20] D.M. Wang, S.I. Shah, J.G. Chen, C.P. Huang, Catalytic reduction of perchlorate by H_2 gas in dilute aqueous solutions, Sep. Purif. Technol. 60 (2008) 14–21.

[21] Z.H. Xue, B. Yin, M.Q. Li, H.H. Rao, H. Wang, X.B. Zhou, X.H. Liu, X.Q. Lu, Direct electrodeposition of well dispersed electrochemical reduction graphene oxide assembled with nickel oxide nanocomposite and its improved electrocatalytic activity toward 2, 4, 6-trinitrophenol, Electrochim. Acta. 192 (2016) 512–520.

[22] D.M. Wang, C.P. Huang, Electrodialytically assisted catalytic reduction (EDACR) of perchlorate in dilute aqueous solutions, Sep. Purif. Technol. 59 (2008) 333–341.

[23] Y.N. Kim, Y.C. Lee, M. Choi, Complete degradation of perchlorate using Pd/N-doped activated carbon with adsorption/catalysis bifunctional roles, Carbon 65 (2013) 315–323.

[24] Y.N. Kim, M. Choi, Synergistic integration of ion-exchange and catalytic reduction for complete decomposition of perchlorate in waste water, Environ. Sci. Technol. 48 (2014) 7503–7510.

[25] R. Mao, X. Zhao, J.H. Qu, Electrochemical reduction of bromate by a Pd modified carbon fiber electrode: kinetics and mechanism, Electrochim. Acta. 132 (19) (2014) 151–157.

[26] Y. Wang, J.H. Qu, R. Wu, P. Lei, The electrocatalytic reduction of nitrate in water on Pd/Sn-modified activated carbon fiber electrode, Water Res. 40 (2006) 1224–1232.

[27] B. Stöhr, H.P. Boehm, R. Schlögl, Enhancement of the catalytic activity of activated carbons in oxidation reactions by thermal treatment with ammonia or hydrogen cyanide and observation of a superoxide species as a possible intermediate, Carbon 29 (1991) 707–720.

[28] P.H. Matter, L. Zhang, U.S. Ozkan, The role of nanostructure in nitrogen-containing carbon catalysts for the oxygen reduction reaction, J.Catal. 239 (2006) 83–96.

[29] W. Chen, F.S. Cannon, J.R. Rangel-Mendez, Ammonia-tailoring of GAC to enhance perchlorate removal I: characterization of NH_3 thermally tailored GACs, Carbon 43 (2005) 573–580.

[30] E.R. Nightingale, Phenomenological theory of ion solvation. Effective radii of hydrated ions, Phys. Chem. 63 (1959) 1381–1387.

[31] W. Chen, F.S. Cannon, J.R. Rangel-Mendez, Ammonia-tailoring of GAC to enhance perchlorate removal II: perchlorate adsorption, Carbon 43 (2005) 581–590.

[32] M. Ran, Z. Xu, H. Lan, H. Liu, J. Qu, Graphene-modified Pd/C cathode and Pd/GAC particles for enhanced electrocatalytic removal of bromate in a continuous three-dimensional electrochemical reactor, Water Res. 77 (2015) 1–12.

[33] S.P. Mezyk, W.J. Cooper, K.P. Madden, D.M. Bartels, Free radical destruction of N-nitrosodimethylamine in water, Environ. Sci. Technol. 38 (2004) 3161–3167.

[34] K.D. Hurley, J.R. Shapley, Efficient heterogeneous catalytic reduction of perchlorate in water, Environ. Sci. Technol. 41 (2007) 2044–2049.

[35] L. Yingwei, R.T. Yang, Hydrogen storage in metal-organic frameworks by bridged hydrogen spillover, J. Am. Chem. Soc. 128 (2006) 8136–8137.

[36] H. Takagi, H. Hatori, Y. Yamada, S. Matsuo, M. Shiraishi, Hydrogen adsorption properties of activated carbons with modified surfaces, J. Alloy. Comp. 385 (2004) 257–263.

[37] G.G. Láng, N.S. Sas, M. Ujvári, G. Horányi, The kinetics of the electrochemical reduction of perchlorate ions on rhodium, Electrochim. Acta. 53 (25) (2008) 7436–7444.

[38] B.P. Chaplin, R. Martin, W.F. Schneider, S. Christoph, J.R. Shapley, T.J. Strathmann, C.J. Werth, Critical review of Pd-based catalytic treatment of priority contaminants in water, Environ. Sci. Technol. 46 (2012) 3655–3670.