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Efficient degradation of ceftriaxone sodium using N-doped carbon xerogel anodes

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ABSTRACT

N-doped carbon xerogel materials were adopted as anodes in the electrochemical oxidation of ceftriaxone sodium (CTRX), a model for cephalosporin in wastewater. A series of melamine-resorcinol-formaldehyde-derived carbon xerogels were synthesized with various amounts of melamine. To analyze the effect of the nitrogen dopant on the structure and composition of the xerogels, N_2-adsorption analysis, X-ray diffraction, X-ray photoelectron spectroscopy, and scanning electron microscopy were used. The CTRX degradation was conducted in a three-electrode structure and the xerogels were prepared as anodes. The results showed that N-doped carbon xerogels had excellent performance for the catalytic degradation of CTRX. The CTRX degradation data were compliant with the first-order kinetic equation and the higher reactivity constant was observed with a higher nitrogen doping level. This implies that the N-doped carbon xerogel is suitable for the electrochemical degradation of cephalosporin.

Keywords: Ceftriaxone sodium; Carbon xerogel; N-doped; Anodic oxidation

1. Introduction

Carbon materials are widely used as electrodes in electrochemical advanced oxidation for the removal of organics in anodic oxidation processes [1]. A variety of carbonaceous materials, such as graphite-based materials [2], carbon fiber [3], carbon nanotubes, black carbon [4], granular activated carbon [5], carbon aerogels [6], and so on, have been applied. The catalytic activity of functional carbon materials is considered beneficial for the effective degradation of organics. Carbon gels (aerogels and xerogels) occupy an important place in the field of functional carbon materials, as a result of their three-dimension network skeleton that can be obtained through simple, template-free sol–gel polycondensation of an organic precursor. Compared to aerogels, xerogels are more easily obtained due to the less complicated drying processes [7].

Heteroatom doping is an important tool to modify the catalytic and electrochemical performance of carbon materials, with nitrogen being one of the most studied dopants [7]. Previous studies have shown that nitrogen doping affects the pore texture, pore size and chemical composition of carbon xerogels derived from resorcinol-formaldehyde (RF) gels [8]. It was indicated that N-doped carbon xerogels (NCXs) could be tailored for suitable applications, such as catalyst supports, better electrochemical performance, energy storage, and so on [9,10].

Remarkable improvements as a result of N doping have been reported in comparison with the pristine carbon materials. Nitrogen doping is considered to enhance the conductivity of the carbon electrode and hence improve the electrochemical performance [11]. The lone pair of electrons of the N atom acts as a donor to enhance electron conduction and the nitrogen doping increases the electron-transfer

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rate due to the electronic modification of the carbon [12]. N-doped graphene-modified cathode materials were found to enhance the catalytic decomposition of phenol [13]. Pd/Pt supported on N-doped activated carbon fiber was reported as a cathode for perchlorate degradation and the nitrogen group promoted the electrocatalytic reduction of perchlorate [14].

Antibiotics are the most important pharmaceuticals for treating microbial infections. Recently, the accumulation of residual antibiotics in water bodies has aroused wide concern. The continuous release of antibiotics into water bodies poses a serious risk to the environment due to aquatic toxicity, development of antibiotic-resistant microorganisms [15]. Cephalosporins belong to a class of beta-lactam antibiotics widely used in human medicine, with the beta-lactam ring being responsible for the antibacterial activity. The β-lactams (cephalosporins and penicillins) are the largest antibiotic category for human use in China [16]. Hydrolysis strongly influences cephalosporin degradation in surface water, and the involved reactions may lead to the formation of still bioactive molecules [17]. Hence, improved cephalosporin wastewater treatment technology is needed.

Electrochemical advanced oxidation processes have been found to be effective for organic wastewater treatment. The performance of anode materials is a key factor influencing pollutant degradation efficiency [18]. To data, limited attention has been focused on reporting on NCXs as anode materials for organic pollutant degradation in electrochemical advanced oxidation processes. Most of these studies focused on the performance of NCXs on electrocatalytic oxygen reduction reactions [10], as well as their application as fuel cells [19,20] and supercapacitors [11] due to their large specific surface and good conductivity.

As aforementioned, the efficient degradation of ceftriaxone sodium (CTRX), as a model for cephalosporin in wastewater, is expected with the NCX anodes. The specific objectives of this work were to integrate NCXs and an electrochemical advanced oxidation process, providing a promising technology for cephalosporin wastewater treatment. A series of melamine-resorcinol-formaldehyde-derived carbon xerogels was synthesized with varying amounts of melamine. The characters of the NCXs were analyzed and applied as anodes to degrade CTRX in an electrochemical advanced oxidation process.

2. Materials and methods

2.1. Synthesis of NCX materials

NCXs were prepared by *in situ* doping involved resorcinol (Macklin, China), melamine (Alfa Aesar, England) and formaldehyde (37% aq. solution, Hangzhou Gaojing, China). Na_2CO_3 (Macklin, China) was used as a catalyst and melamine was the nitrogen source. To study the effect of the melamine on the character of the xerogels, the *R*/*F* molar ratio was fixed at 0.5 and the *R*/*C* molar ratio was fixed at 500. The pH was adjusted to 6.0–6.5. While the *M*/*R* molar ratios used were 0.008, 0.04, and 0.08 to make N-doping levels (wt.%) at 0.1%, 0.5%, and 1%, entitled CXN-0.1, CXN-0.5, and CXN-1 (Table 1), respectively. RF gels without melamine were synthesized for comparisons, entitled CX.

The gelation was performed at 25°C for 1 d, 50°C for 2 d, and 80°C for 5 d, and then carbon xerogels were obtained from dried gels by pyrolysis at 800°C for 2 h under a N_2 atmosphere (400 mL/min) in a tubular oven. Then, the xerogels were milled with a mesh size from 150 to 200.

2.2. Characterization of NCX materials

The textural characterization of the xerogels was based on the nitrogen adsorption/desorption isotherms determined at 77 K with an ASAP2020 analyzer (Micromeritics, U.S.A.). The apparent surface area S_{BET} was calculated by the Brunauer–Emmett–Teller (BET) model and the pore size in the mesopore range was calculated by the Barrett–Joyner–Halenda method [10]. The X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance apparatus (40 kV and 40 mA). Scanning electron microscopy (SEM) images were obtained by a FEI QUANTA Q400 scanning electron microscope. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo ESCALAB 250Xi apparatus.

2.3. Experimental setup

The anodes were prepared by mixing the prepared NCX power (80 wt.%), carbon black (Shenzhen, Ruiheda, China, 10 wt.%), and polyvinylidene fluoride (MW = 275,000, Sigma-Aldrich, USA, 10 wt.%) in dimethylacetamide (DMAc, Adamas, China) to form a black slurry [5]. Then, the slurry was painted onto a piece of carbon paper and dried at 80°C for 6 h. The area of carbon paper covered with slurry was 1.5 cm^2. Each electrode contained 6–7 mg of NCX material.

Electrochemical measurements proceeded with an electrochemical analyzer (CHI600E, Chenhua, China). Electrooxidation processes were carried out in a cylindrical reactor containing 50 mL of solution with magnetic stirring. The anode was the working electrode, a platinum plate (1 cm^2) and a Ag/AgCl electrode were adopted as the counter and reference electrodes, respectively. In the CTRX degradation experiments, the initial concentration of CTRX was 10 mg/L and the current density was 2 mA/cm^2. The area of the working electrode was 1.5 cm^2 and the gap between working and counter electrodes was 2 cm. K_2SO4 (2 mM) was added as supporting electrolyte to increase the conductivity.

2.4. Analytical procedure

CTRX (CAS104376-79-6) was purchased from Tokyo Chemical Industry. CTRX was quantitative analyzed via high-performance liquid chromatography (HPLC, 2010HT, Shimadzu, Japan) equipped with a C18 analytical column and an ultraviolet detector at 254 nm. The HPLC was operated under a mobile phase ratio of methyl alcohol: 0.2% phosphoric acid = 30:70 and a flow rate of 1 mL/min. The oven temperature was 25°C and the injection volume was 20 μL.

3. Results and discussion

3.1. Characterization of NCXs

Fig. 1 shows the N_2 adsorption–desorption isotherms of the xerogels. In addition, the textural parameters of the

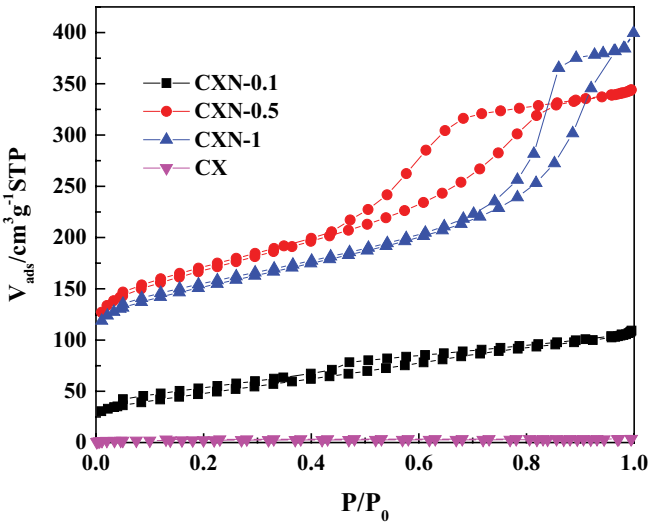

Fig. 1. Nitrogen adsorption-desorption isotherms for carbon xerogels.

NCX samples, including specific surface, pore volume and pore diameter, are summarized in Table 1. The series display different adsorption–desorption isotherms depending on different *M*/*R* ratios. An obvious hysteresis loop can be seen for NCXs with higher *M*/*R* ratios (CXN-0.5 and CXN-1). The increase in N_2 uptake with growing pressure of CXN-1 implies a high surface area due to the presence of interconnected nanoparticles [7]. The shape of the isotherms are type IV hysteresis and it is deduced that the samples are mainly mesoporous [21].

As the *M*/*R* ration decreases, the loop shrinks, indicating a decrease in pore volume. This is further confirmed by the calculation of V_{mes}, without N doping yielding a material with poorly developed porosity. The isotherm of CX is nearly a straight line, indicating a very small specific surface area. From Table 1, it can be clearly seen that N doping has a strong influence on the pore texture of carbon xerogels. The S_{BET} increases with the increase of melamine reaching the maximum of 566.83 m^2/g in CXN-0.5, and decreases to 509.06 m^2/g in CXN-1. It was partial according to the study of Lu et al. [11] who considered the specific surface area of carbon xerogel decrease with the increase of melamine.

To further understand the structure and the chemical state of nitrogen, XPS analysis was applied. XPS spectra can be used to identify chemical elements in materials. All the NCX samples exhibit a similar signal in XPS. Fig. 2 illustrates the survey and the N1s spectra of the CXN-1 sample. No signal of nitrogen can be detected in the spectra of CX, as it was prepared without melamine.

The XPS full survey of CXN-1 shows three major peaks at 284.6, 400.6, and 531.6 eV corresponding to C1s, N1s, and O1s, respectively [22]. The deconvolution of the N1s band indicates the presence of at least three different components for the N atom, which could be assigned to oxidized N (407.2 eV), graphitic N (401.1 eV), and pyridinic N (398.2 eV) [23], respectively. Pyridinic-N is a critical and active site in the oxygen reduction reaction [24]. The N at.% values derived from the XPS composition are summarized

Table 1
Textural parameters of NCXs

Sample	S_{BET} (m^2/g)	V_{mes} (m^3/g)	*D* (nm)	*N* %xps	*M*/*R*
CXN-0.1	170.25	0.16	3.88	1.69	0.008
CXN-0.5	566.83	0.45	3.74	2.75	0.04
CXN-1	509.06	0.50	4.75	2.48	0.08
CX	7.9961	0.004	3.48	–	–

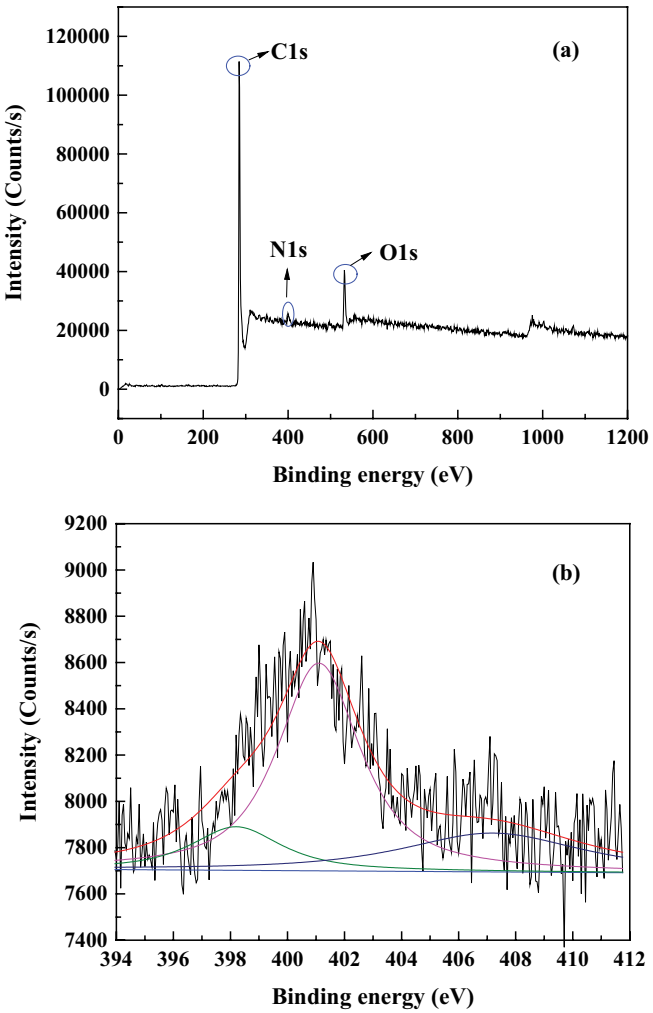

Fig. 2. XPS spectra of (a) survey scan and (b) N1s for CXN-1.

in Table 1. For the CX-0.1 sample (low melamine dried gels), the N at.% was minor. However, the XPS-derived N at.% are not directly proportional to the bulk value for CX-0.5 and CX-1 samples. Since XPS is a surface analysis, it could underestimate or overestimate its bulk value [8]. The inhomogeneous surface and bulk composition derived from the XPS N at.%, indicating a heterogeneous distribution of the functional groups [10]. A loss of heteroatoms is inevitably caused by carbonization of organic matter [7], and the melamine and resorcinol react with formaldehyde at different speeds [8].

Fig. 3 reveals the XRD patterns of the xerogels. The two diffraction peaks at 25° and 43° could be attributed to the graphitic characteristics of the (002) and (100) planes, respectively. The relatively broad peaks indicate that these nitrogen-doped carbon materials are amorphous essentially [25].

The structures at microscopic length scales are shown in the SEM images of the carbon xerogels synthesized with different contents of melamine (Fig. 4). Samples display the more obvious porous structure with increasing melamine content. By increasing the *M*/*R* ratio, the large opened network and the loose structure were clearly observed by SEM. The samples show an inter-connected work formed by aggregate-fused carbon nanoparticles.

CX, being prepared without melamine, has minor specific surface area, as indicated by Table 1. The minor specific surface area of CX may be caused by the dense structure according to the SEM image. Further addition of melamine in precursor caused more obvious pores in sample CXN-0.5 and CXN-1. This phenomenon corresponds to the study of Lu et al. [11].

3.2. Degradation of CTRX

To investigate the influence of nitrogen doping on the anode during the CTRX degradation process, a series of experiments was conducted with different NCX anodes. The results are shown in Fig. 5. The CTRX electrical degradation efficiency varied with different anodes.

The degradation results indicate that nitrogen doping favored the electrical degradation of CTRX. The total pore volume and BET specific surface of CXN-1 and CXN-0.5 are larger than those of CXN-0.1 and CX. The larger BET specific surface area could provide a larger active area to accelerate the generation of active radicals and benefit the degradation of CTRX. Furthermore, the best catalytic activity

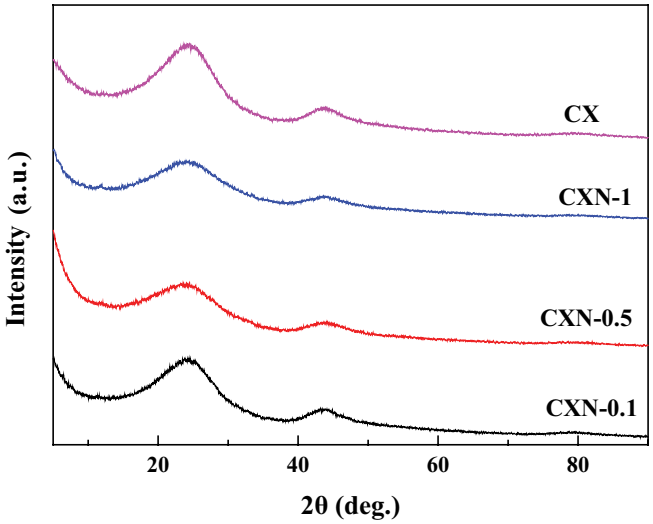

Fig. 3. XRD patterns of N-doped carbon xerogels.

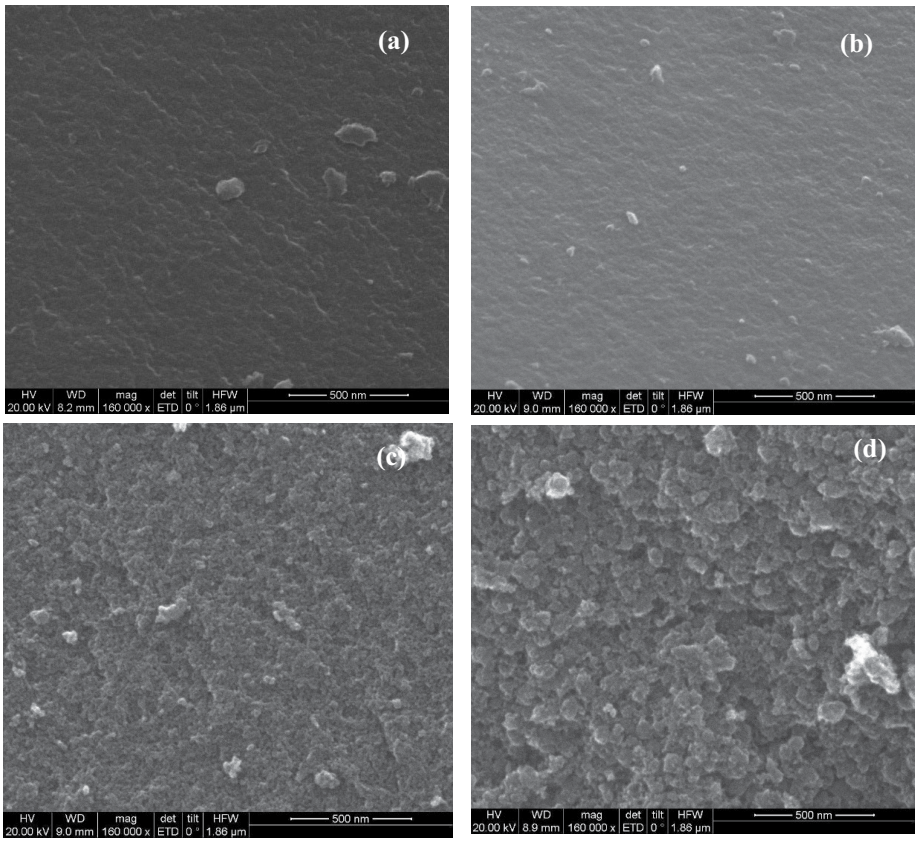

Fig. 4. SEM images of carbon xerogels, (a) CX, (b) CXN-0.1, (c) CXN-0.5, and (d) CXN-1.

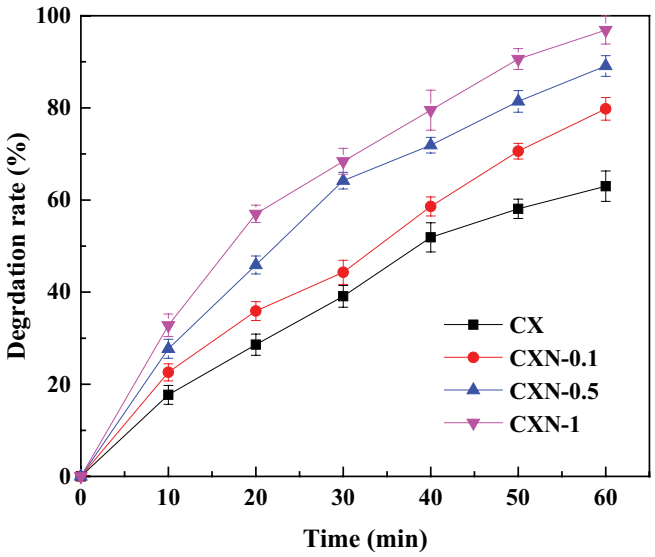

Fig. 5. Electro-catalytic degradation of CTRX by carbon xerogel anodes.

was observed for the CXN-1 anode, which had a lower surface area than CXN-0.5. This is due to the nitrogen dopant in the carbon xerogel anodes producing more active sites for the electrochemical reduction of O_2 [18].

The mechanism of the enhancement of ORR activities by nitrogen-doped carbon materials is not yet clearly understood. This effect could be related to the acid-base properties of the nitrogen functional groups, which involve ionic charge exchange from the surface to the electrode by proton transfer from or to pyridinic and pyrrolic groups [26].

In addition, the degradation curves were fitted by a pseudo-first-order kinetic equation and the parameters including rate constant k and coefficient R^2 are listed in Table 2. The model is expressed as follows:

$$-\ln\left(\frac{C_t}{C_0}\right) = kt \quad (1)$$

where C_t is the CTRX residual concentration (mg/L), C_0 is the initial concentration of CTRX (mg/L), t is the reaction time (min), and k is the reactivity constant (min^{-1}) [18].

To determine the economic viability, the energy efficiency was calculated by the following Eq. (2) [27]:

$$\text{Energy efficiency (mg/Wh)} = \frac{m}{U \times I \times t} \quad (2)$$

where m is the amount of CTRX degraded (mg), U is the average applied voltage (V), I is the electrolysis current (A), and t is the time for degradation treatment (h).

The R^2 value in various anode degradation processes ranged from 0.98542 to 0.99695 (Table 2), indicating that the electrical degradation of CTRX by NCXs anodes was compliant with the mathematical model of the first-order kinetic equation. The rate constant k of CXN-1 anode for CTRX removal was far higher than that of CX anode. The high

Table 2
First-kinetic fitting parameters for CTRX degradation with different anodes

Anode material	Rate constants (k, min^{-1})	Coefficient (R^2)	Energy efficiency (mg/Wh)
CX	0.01725	0.99621	40.4
CXN-0.1	0.02306	0.98542	61.9
CXN-0.5	0.03304	0.99695	73.9
CXN-1	0.04173	0.99316	95

energy efficiency was observed with the CXN-1 anode. The results indicate that the N dopant benefits the CTRX degradation due to relatively high degradation efficiency and a rapid reduction rate.

4. Conclusion

The effects of a N-doped electrode in electro-oxidation process on the CTRX degradation were demonstrated in this study. NCXs were prepared by tuning the M/R ratio during the polymerization process via a sol–gel method. The results indicated that the pore texture and structure of xerogels could be tailored by the nitrogen dopant. A three-electrode structure was applied and the electro-oxidation efficiency of the anodes made of those synthesized materials (CX, CX-0.1, CX-0.5, and CX-1) had been investigated for the degradation of antibiotic CTRX. The best degradation performance, reduction rate and energy efficiency were observed for the highest N-doping level anode, suggesting its application potential in cephalosporin wastewater treatment.

Acknowledgments

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References

[1] M.X. Qiao, Y. Zhang, L.F. Zhai, M. Sun, Corrosion of graphite electrode in electrochemical advanced oxidation processes: degradation protocol and environmental implication, Chem. Eng. J., 344 (2018) 410–418.
[2] P.V. Nidheesh, Graphene-based materials supported advanced oxidation processes for water and wastewater treatment: a review, Environ. Sci. Pollut. Res., 24 (2017) 27047–27069.
[3] S.H. Cho, A. Jang, P.L. Bishop, S.H. Moon, Kinetics determination of electrogenerated hydrogen peroxide (H_2O_2) using carbon fiber microelectrode in electroenzymatic degradation of phenolic compounds, J. Hazard. Mater., 175 (2010) 253–257.
[4] H. Song, L. Yan, J. Jiang, J. Ma, S. Pang, X. Zhai, W. Zhang, D. Li, Enhanced degradation of antibiotic sulfamethoxazole by electrochemical activation of PDS using carbon anodes, Chem. Eng. J., 344 (2018) 12–20.
[5] Y. Li, Y. Jiang, T.J. Wang, C. Zhang, H. Wang, Performance of fluoride electrosorption using micropore-dominant activated carbon as an electrode, Sep. Purif. Technol., 172 (2017) 415–421.

[6] Y. Wang, Z. Pan, D. Qin, S. Bai, Q. Peng, Preparation of Ce-TiO_2/carbon aerogel electrode and its performance in degradation of 4-chlorophenol, J. Rare Earth., 36 (2018) 374–378.
[7] W. Kiciński, M. Norek, B.J. Jankiewicz, Heterogeneous carbon gels: N-doped carbon xerogels from resorcinol and N-containing heterocyclic aldehydes, Langmuir, 30 (2014) 14276–14285.
[8] D. Salinas-Torres, A.F. Léonard, V. Stergiopoulos, Y. Busby, J.J. Pireaux, N. Job, Effect of nitrogen doping on the pore texture of carbon xerogels based on resorcinol-melamine-formaldehyde precursors, Microporous Mesoporous Mater., 256 (2018) 190–198.
[9] R.P. Rocha, J. Restivo, J.P.S. Sousa, J.J.M. Órfão, M.F.R. Pereira, J.L. Figueiredo, Nitrogen-doped carbon xerogels as catalysts for advanced oxidation processes, Catal. Today, 241 (Pt A) (2015) 73–79.
[10] B. Nagy, S. Villar-Rodil, J.M.D. Tascón, I. Bakos, K. László, Nitrogen doped mesoporous carbon aerogels and implications for electrocatalytic oxygen reduction reactions, Microporous Mesoporous Mater., 230 (2016) 135–144.
[11] C. Lu, Y.H. Huang, J.S. Hong, Y.J. Wu, J. Li, J.P. Cheng, The effects of melamine on the formation of carbon xerogel derived from resorcinol and formaldehyde and its performance for supercapacitor, J. Colloid Interface Sci., 524 (2018) 209–218.
[12] J. Li, S. Yun, X. Zhou, Y. Hou, W. Fang, T. Zhang, Y. Liu, Incorporating transition metals (Ta/Co) into nitrogen-doped carbon as counter electrode catalysts for dye-sensitized solar cells, Carbon, 126 (2018) 145–155.
[13] W. Yang, M. Zhou, L. Liang, Highly efficient in-situ metal-free electrochemical advanced oxidation process using graphite felt modified with N-doped graphene, Chem. Eng. J., 338 (2018) 700–708.
[14] F. Yao, Y. Zhong, Q. Yang, D. Wang, F. Chen, J. Zhao, T. Xie, C. Jiang, H. An, G. Zeng, X. Li, Effective adsorption/electrocatalytic degradation of perchlorate using Pd/Pt supported on N-doped activated carbon fiber cathode, J. Hazard. Mater., 323 (2017) 602–610.
[15] X. Yu, X. Tang, J. Zuo, M. Zhang, L. Chen, Z. Li, Distribution and persistence of cephalosporins in cephalosporin producing wastewater using SPE and UPLC-MS/MS method, Sci. Total Environ., 569–570 (2016) 23–30.
[16] Q.Q. Zhang, G.G. Ying, C.G. Pan, Y.S. Liu, J.L. Zhao, Comprehensive evaluation of antibiotics emission and fate in the river basins of China: source analysis, multimedia modeling, and linkage to bacterial resistance, Environ. Sci. Technol., 49 (2015) 6772–6782.
[17] A.R. Ribeiro, B. Sures, T.C. Schmidt, Cephalosporin antibiotics in the aquatic environment: a critical review of occurrence, fate, ecotoxicity and removal technologies, Environ. Pollut., 241 (2018) 1153–1166.
[18] K. Li, Z. Rong, Y. Li, C. Li, Z. Zheng, Preparation of nitrogen-doped cotton stalk microporous activated carbon fiber electrodes with different surface area from hexamethylenetetramine-modified cotton stalk for electrochemical degradation of methylene blue. Results Phys., 7 (2017) 656–664.
[19] A. Sarapuu, K. Kreek, K. Kisand, M. Kook, M. Uibu, M. Koel, K. Tammeveski, Electrocatalysis of oxygen reduction by iron-containing nitrogen-doped carbon aerogels in alkaline solution, Electrochim. Acta, 230 (2017) 81–88.
[20] S.S. Liu, H.M. Zhang, Z. Xu, H.X. Zhong, H. Jin, Nitrogen-doped carbon xerogel as high active oxygen reduction catalyst for direct methanol alkaline fuel cell, Int. J. Hydrogen Energy, 37 (2012) 19065–19072.
[21] M.R. Carrasco-Díaz, E. Castillejos-López, A. Cerpa-Naranjo, M.L. Rojas-Cervantes, On the textural and crystalline properties of Fe-carbon xerogels. Application as Fenton-like catalysts in the oxidation of paracetamol by H_2O_2, Microporous Mesoporous Mater., 237 (2017) 282–293.
[22] Z.X. Cai, X.H. Song, Y.Y. Chen, Y.R. Wang, X. Chen, 3D nitrogen-doped graphene aerogel: a low-cost, facile prepared direct electrode for H_2O_2 sensing, Sens. Actuators B, 222 (2016) 567–573.
[23] J.S. Han, D.Y. Chung, D.G. Ha, J.H. Kim, K. Choi, Y.E. Sung, S.H. Kang, Nitrogen and boron co-doped hollow carbon catalyst for the oxygen reduction reaction, Carbon, 105 (2016) 1–7.
[24] C. He, L. Li, T. Zhang, F. Sun, C. Wang, Y. Lin, Nitrogen-doped amorphous carbon with effective electrocatalytic activity toward oxygen reduction reaction, Mater. Res. Bull., 84 (2016) 118–123.
[25] N. Liu, L. Ding, H. Li, M. Jia, W. Zhang, N. An, X. Yuan, N-doped nanoporous carbon as efficient catalyst for nitrobenzene reduction in sulfide-containing aqueous solutions, J. Colloid Interface Sci., 490 (2017) 677–684.
[26] V. Perazzolo, C. Durante, A. Gennaro, Nitrogen and sulfur doped mesoporous carbon cathodes for water treatment, J. Electroanal. Chem., 782 (2016) 264–269.
[27] Y. Wang, C. Shen, M. Zhang, B.T. Zhang, Y.G. Yu, The electrochemical degradation of ciprofloxacin using a SnO_2-Sb/Ti anode: influencing factors, reaction pathways and energy demand, Chem. Eng. J., 296 (2016) 79–89.