Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2012.749373

51 (2013) 3489–3496
April

Taylor & Francis
Taylor & Francis Group

Effects of ageing and incorporation of ion-exchange membrane on the electrosorption performance of activated carbon based electrodes modules

Zhaolin Chen[a], Hongtao Zhang[a,*], Chun Yang[b], Xiaowei Sun[b], Hongfei Guo[b], Chunxu Wu[a], Fangqin Xue[a], Lei Gao[a]

[a]*School of Environment, Tsinghua University, Beijing 100084, China*
Tel. +86 10 6279 7240; Fax: +86 10 6279 2625; email: 51green@sohu.com
[b]*EST Purification Equipment Research Center, Beijing 100176, China*

Received 1 April 2012; Accepted 23 August 2012

ABSTRACT

The effects of ageing and incorporation of ion-exchange membrane on the electrosorption performance of activated carbon (AC) electrodes-based electrosorption modules were investigated. It was found that the surface area of aged electrode decreased while the average pore size increased. In addition, more surface functional groups, especially –COOH groups were created on the electrode surface due to ageing. All these lead to a decrease in the electrosorption capacity and electrosorption rate. Incorporation of ion-exchange membranes can improve the desalination performance of the electrosorption module, especially for the aged electrode.

Keywords: Ageing; Electric double layers (EDLs); Electrosorption; Functional groups; Ion-exchange membrane

1. Introduction

Water shortage has become one of the major problems all over the world. It is generally recognized that seawater desalination is a very attractive solution to this problem. There are many desalination technologies which can remove ions from brackish solution. Conventional desalination technologies, such as ion exchange, thermal distillation, reverse osmosis, electric dialysis, etc. [1–3] have issues in maintenance, complex pretreatment, high temperature and high energy-consumption [2,4].

Electrosorption is defined as potential-induced adsorption of ions onto the surface of charged electrode. When an electrical potential is conducted to an electrode, charged ions migrate to the electrode and create electric double layers (EDLs). Once the external field is removed, the adsorbed ions are quickly released back to the bulk solution [5]. Compared with the conventional desalination technologies, electrosorption is an energy-efficient desalination process due to the fact that it operates at a low electrode potential (about 1–1.5 V) at which no electrolysis reactions occur [6]. In addition, this process is environmentally friendly because it does not require chemicals for regeneration [7–9]. Materials, such as activated carbon, carbon aerogel, carbon nanofibers and carbon nanotubes can be used as the electrosorption electrode [10–15]. Although carbon aerogel, carbon nanofibers and carbon nanotubes have excellent electrosorption performance, the manufacturing

---

*Corresponding author.

process of these materials is complicate and mass production is expensive. Therefore, it is difficult to utilize these materials for industrial applications. Activated carbon (AC) is the most competitive electrode material for industrial application at present due to its large specific surface area, easy availability as raw material and low cost [14].

One major drawback of the electrosorption technology is that the electrosorption capacity of the electrosorption module decreases along the carbon electrode ageing [16,17]. With the ageing of carbon electrode, the porous texture of the carbon material and the electrical contact resistance will be changed. Furthermore, surface oxygen groups will be created on the surface of the carbon electrode [18]. Surface oxygen groups can change the pseudo-capacity of the carbon electrode [19], also bring about the decrease in the electrosorption capacity and the charge efficiency [16,20]. The electrosorption does not have high Coulombic efficiency, which is defined by the amount of ions removed per amount of charge. Once the electrode is saturated with ions, it has to be electronically discharged by shunting the electrode terminals, which allow the ions to re-enter the bulk solution [21]. In order to solve these problems, the "Charge Barrier" Flow Through Capacitor was invented by Marc Andelman in 2000 [22]. By adopting selective layers, such as ion-exchange membrane, the charge efficiency can be substantially improved.

In this study, the effects of electrode ageing on the performance of activated carbon-based electrodes modules will be investigated. The causes of these effects will be explored from the changes in the morphology and electrochemical characteristics of the electrode and the surface functional groups during the ageing process. Especially, incorporation of ion-exchange membrane will be proposed as a solution to reverse the negative effects of ageing. Its effectiveness will be experimentally validated and the mechanism behind this will be explored as well.

2. Materials and method

2.1. Electrosorption and membrane electrosorption

Adsorption experiments were carried out in a flow-through system as depicted in Fig. 1. The system consisted of a water tank, a peristaltic pump, an electrosorption module, a conductivity meter, and a rectifier. AC electrodes were composed of activated carbon powder and were supplied by the Beijing EST research institute. The electrosorption module consisted of two electrodes separated by a nylon spacer. Each assembled electrode had an area of $150 \times 1800\,\text{mm}^2$ with a thickness of 1.3 mm. The distance between the two electrodes was 1.5 mm. The conductive layer was graphite paper with a thickness of 0.3 mm. AC electrode was pasted on the graphite paper with conductive adhesive (poly tetra fluoro ethylene and conductive carbon black). Aqueous KCl solution was used for the experiments and the flow rate of the peristaltic pump was kept at 100 mL/min. The polarity was changed after each cycle. Electrosorption module 1 was aged at 1.5 V for 225 days (3600 cycles, each cycle consisted of 45 min of electrosorption and 45 min of regeneration), the electrosorption performance of electrosorption module 1 had been tested before ageing. When the electrochemical ageing of the electrodes was achieved, the electrodes were removed from module 1, and incorporated (together with ion-exchange membranes) into the membrane electrosorption module 2 as depicted in Fig. 2. The characteristics of ion-exchange membranes are listed in Table 1.

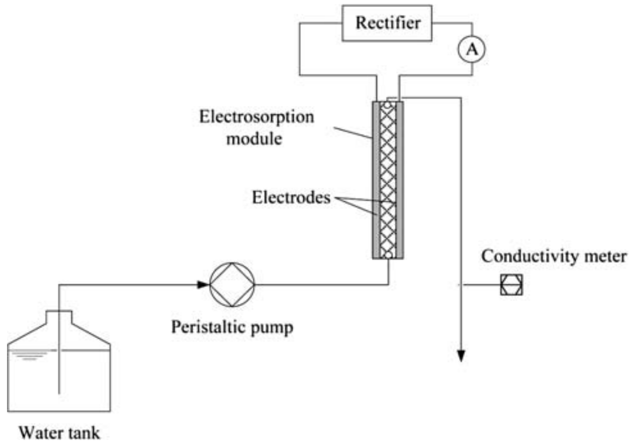


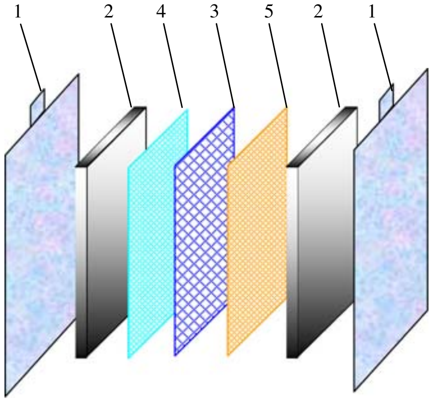
Fig. 1. Diagram of adsorption experiments.

Additionally, another membrane electrosorption module 3 was prepared with fresh electrodes. Electrosorption and membrane electrosorption were conducted under constant potential conditions (1.5 V). A rectifier maintained a constant voltage between the two electrodes during adsorption. KCl concentration was measured by a conductivity meter (Shanghai Leici, DDS-307A).

After the electrosorption experiments, the electrodes were removed from module 1 and module 2 and washed with deionized water before they were analyzed for morphology, surface functional groups and electrochemical characteristics.

2.2. Morphology observation

The morphology of fresh AC electrode was analyzed with a scanning electron microscope (SEM) (Hitachi S-3400N). The Brunauer–Emmett–Teller (BET)



1-Conductive layer; 2-Electrode; 3-Separator; 4-Anion exchange membrane (AEM);
5-Cation exchange membrane (CEM)

Fig. 2. Diagram of membrane electrosorption module.

Table 1
Characteristics of ion-exchange membranes

Characteristics	Anion exchange membrane	Cation exchange membrane
Thickness (mm)	0.75	0.75
Chemical stability (pH)	1–10	1–10
Type	Na-type	Cl-type
Surface resistance ($\Omega\,cm^2$)	15	20

specific surface areas of AC electrodes were determined by using a surface analyzer (Micromeritics ASAP 2020) with nitrogen (99.99% purity) adsorption/desorption at 77 K. Prior to nitrogen adsorption, the adsorbents were degassed under vacuum at 423 K for 6 h.

2.3. Surface functional groups determination

Surface functional groups on the electrodes were determined by acid–base titration method as described by Boehm [23]. An AC electrode sample (1.0 g) was placed in containers with 100 mL of the following solutions respectively: sodium bicarbonate ($NaHCO_3$), sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH). The concentration of the aqueous solutions was 0.02 M. The containers were sealed with rubber caps and shaken for 24 h at 298 K. After that the resulting suspensions were filtered and 10 mL of the accurately withdrawn aliquot of filtrates were titrated up to pH 4.0 by 0.02 M hydrochloric acid in order to estimate the residual base. The titration value was measured three times for each sample and then the amount of functional groups was calculated using the average of the three titration data.

2.4. Electrochemical characterization of AC electrodes

The electrochemical performance of AC electrodes was evaluated by cyclic voltammetry (CV) using an electrochemical workstation (Princeton PARSTAT 4000). The AC electrodes, Pt plate and Ag/AgCl were used as the working electrode, counter and reference electrode, respectively. Cyclic voltammetry was performed at a sweep rate of 10 mV/s with a potential range of −1.2 to 1.2 V at ambient temperature. During a cyclic voltammetric measurement, the aqueous electrolyte was 1 mol/L NaCl. The resistivity of AC electrodes was determined by an Electronic multimeter (Peking SH3-DT9508B).

3. Results and discussion

3.1. Electrosorption performance

Electrosorption experiments of the fresh AC electrode and the aged electrode were conducted by supplying a solution of 1020 mg/L of KCl at a flow rate of 100 mL/min. After applying a potential of 1.5 V for 45 min, the circuit was immediately shorted for 45 min. Fig. 3 shows the concentration of the effluent for each module. As can be seen in Fig. 3, desalination occurred more efficiently with the fresh electrodes than with the aged electrodes. When the potential was applied, ions were quickly electro-sorbed, so that the concentrations decreased from the initial 1020 mg/L to the minima of 212 and 287 mg/L for the fresh electrode and the aged electrode, respectively. The

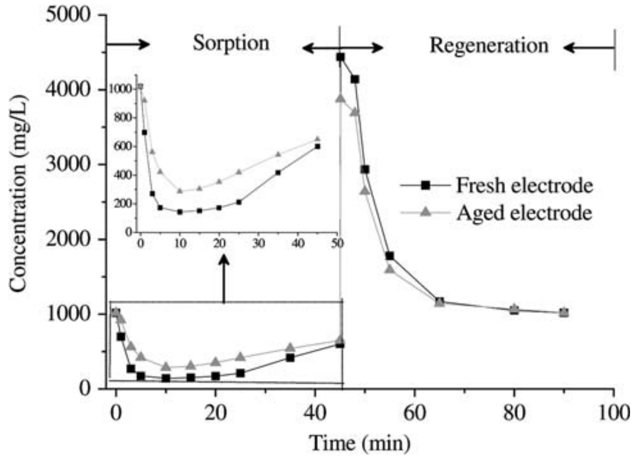


Fig. 3. The electrosorption effluent of different AC electrodes (1.5 V).

average concentrations of the effluent during the electrosorption period were 307 and 490 mg/L for fresh electrode and aged electrode, respectively. The electrosorption capacity of the fresh electrode was 10.22 mg/g, which decreased to 7.63 mg/g for the aged electrode. These results demonstrate that the desalination efficiency was decreased by electrochemical oxidization.

During the regeneration process, the concentration increased steeply when the circuit was shorted, showing peak values of 4,442 and 3,876 mg/L for the fresh electrode and the aged electrode, respectively. Especially for the fresh electrode, this was around a fourfold increase of the raw solution. Most of the ions were desorbed within 10 min after the circuit was shorted. Because desorption proceeded rapidly, it was easy to regenerate the electrode during the process operation, meaning that it should be possible to increase the recovery ratio of the feed solution by reducing the regeneration time.

The electrosorption and membrane electrosorption effluent of the fresh electrode and the aged electrode is show in Figs. 4 and 5. As can be seen in Fig. 4, desalination occurred more efficiently with the ion-exchange membrane than without ion-exchange membrane. The electrosorption capacity of the fresh electrode was 10.22 mg/g without the ion-exchange membrane, which increased to 10.66 mg/g with the ion-exchange membrane (increased by 4.5%). From Fig. 4, it was found that the electrosorption capacity of the aged electrode was 7.63 mg/g without the ion-exchange membrane, which increased to 9.58 mg/g with the ion-exchange membrane (increased by 25.6%). It can be concluded that membrane electrosorption improves desalination efficiency, especially for the aged electrode.

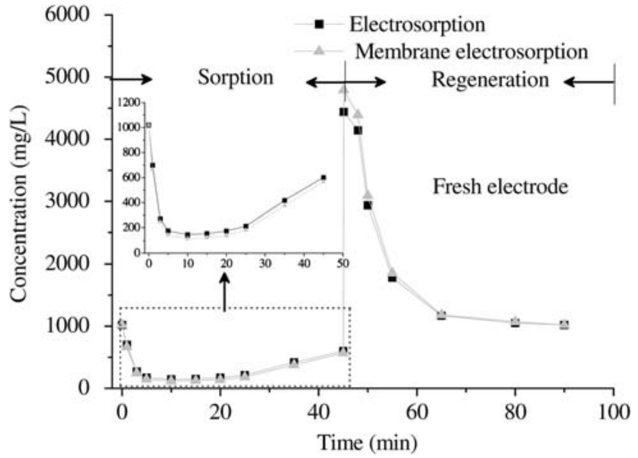


Fig. 4. The electrosorption and membrane electrosorption effluent of fresh electrode (1.5 V).

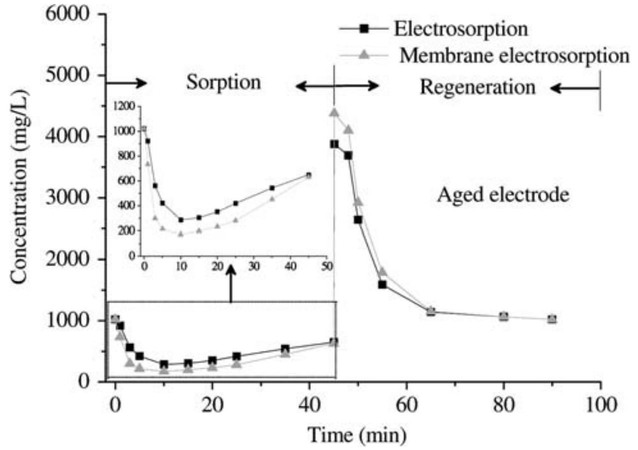


Fig. 5. The electrosorption and membrane electrosorption effluent of aged electrode (1.5 V).

3.2. Microstructural changes in the aged AC electrodes

Fig. 6 is a SEM image of fresh AC electrode, which shows that the fresh AC electrode is a continuous, irregular network-like porous material. Fig. 7 shows the nitrogen adsorption isotherms of the fresh electrode and aged electrode. The measured microstructure characteristics such as BET, surface area, pore size, and pore volumes of the two electrodes are listed in Table 2. In contrast, electrochemical ageing had some influence on the microstructure and pore structure. The relative volume of the pores in various pore sizes ranges can be obtained from the histogram, as shown in Fig. 8. The histograms indicated a sharp maximum at about 2–2.5 nm. It was suggested that the pore size was mainly that of mesopores (2–50 nm). According to the previous studies, mesopores are

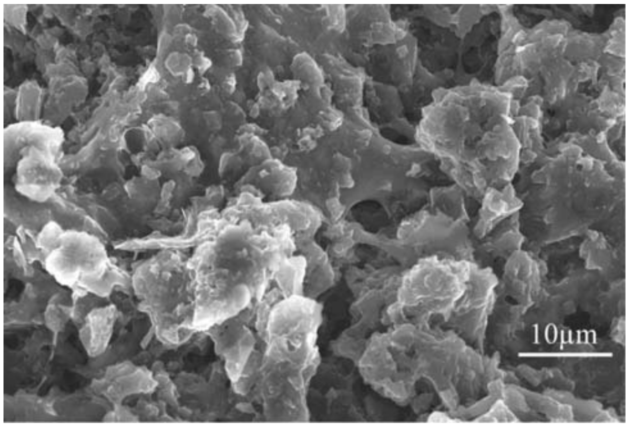


Fig. 6. SEM image of fresh AC electrode.

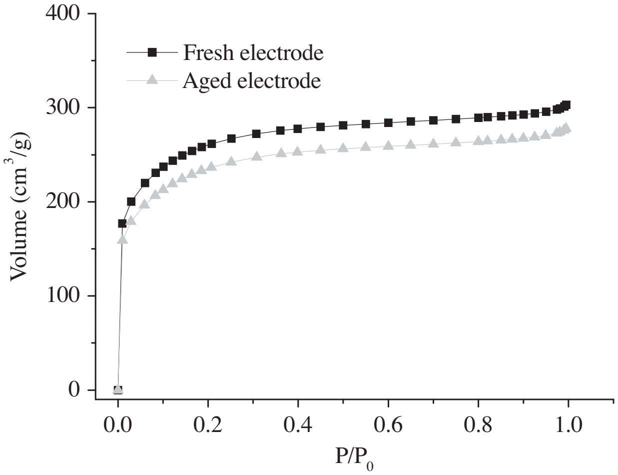


Fig. 7. Adsorption isotherms of fresh electrode and aged electrode.

beneficial to the adsorption of ions, whereas micropores (<2 nm) are not beneficial due to the electric double layer overlapping effects [13]. Therefore, the AC electrodes obtained in this study are ideal to study the electrosorption related experiments.

After electrochemical ageing, the aged electrode showed structure changes. There were losses in porosity, especially in the micropore area. The average pore size increased from 2.26 to 2.28 nm. But there were no significant changes in the mesopore and macropore area. The porous texture change in the aged AC electrodes could be a consequence of the combination of the direct oxidation by the anodically polarized electrode according to Eqs. (1) and (2) [24], and the indirect oxidation by electrogenerated oxidant species, such as hydroxyl radicals according to Eqs. (3) and (4) [25].

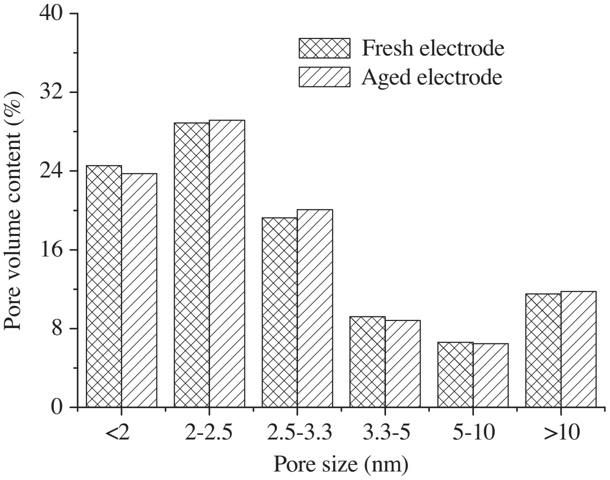


Fig. 8. Pore size distribution of fresh electrode and aged electrode.

$$C + H_2O \rightarrow C\text{–}O + 2H^+ + 2e^- \quad (1)$$

$$C + H_2O \rightarrow C\text{–}OH + H^+ + e^- \quad (2)$$

$$H_2O \rightarrow HO^\bullet + H^+ + e^- \quad (3)$$

$$OH^- \rightarrow OH^\bullet + e^- \quad (4)$$

In the case of cathodic polarization, the direct reduction (Eq. (5)) [24] by the electrode potential may be responsible for the change in the porous texture.

$$C + H_2O + e^- \rightarrow C\text{–}H + OH^- \quad (5)$$

3.3. Changes of surface groups on the AC electrodes surfaces during ageing

Table 3 shows the measured surface functional groups of the AC electrodes. After electrochemical

Table 2
Pore characteristics of fresh electrode and aged electrode

Sample	BET surface (m^2/g)	Micropore surface area (m^2/g)	Total volume (m^3/g)	Average pore size (nm)
Fresh electrode	828	336	0.46	2.26
Aged electrode	753	275	0.42	2.28

ageing, the total surface functional groups of the aged electrode showed significant increase. The –COOH groups of the aged electrode increased from 0.027 to 0.391 mmol/g. The –COOR groups of the aged electrode increased from 0.006 to 0.197 mmol/g. The –OH groups of the aged electrode decreased from 0.039 to 0.011 mmol/g. It can be seen that electrode ageing creates more surface functional groups, especially –COOH groups.

3.4. Electrochemical characteristics of AC electrodes

In order to check the changes in the electrochemical properties of the aged electrodes, cyclic voltammetric studies of the fresh electrode and the aged electrode were carried out. Cyclic voltammograms (CVs) of fresh electrode and the aged electrode obtained in 1 mol/L NaCl solutions at a scan rate of 10 mV/s, with a potential range of −1.2 to 1.2 V vs. Ag/AgCl, are given in Fig. 9. After electrochemical ageing, the aged electrode showed capacity loss resulting from high internal resistance and pore blockage characteristics. It is well known that the oxygen functional groups are mainly located at the edges of the basal planes and the entrance of the pores in activated carbons [26]. Besides, the oxygen functional groups are ideal sites for water adsorption, favoring the creation of water clusters at the entrance of the pores and blocking of access of the electrolyte ions down into their double-layer interfaces. The observed decrease in voltammetric charges in the aged electrodes direction proved the oxidation of AC electrodes by long time electrosorption. The resistivity of the fresh electrode and the aged electrode was 9.5 and 21.4 Ω cm, respectively, which indicated the increase in electrode resistance due to the creation of oxygen functional groups during the ageing process.

3.5. Enhancement of electrosorption performance with ion-exchange membrane

That ion-exchange membrane can improve desalination efficiency could be explained with the adsorption and desorption mechanism of ions on the electrode surface. Fig. 10(a) shows the transport of ions when a potential is applied to a pair of electrodes. At the anode surface, anions are adsorbed; however, some cations are expelled and immediately adsorbed by the cathode, which will decrease the desalination efficiency. When the circuit is shorted (Fig. 10(b)), the anions in the EDL move back to the bulk solution from the anode surface to re-establish electro-neutrality, which lead to desorption of ions; however, some cations from the bulk solution could move to the EDL by electrostatic force. Though the EDL will disappear at the end of regeneration, if there are many functional groups on the electrode surface, ions may be adsorbed by those functional groups. This will decrease the electrosorption efficiency of the next cycle. Fig. 10(c) shows the transport of ions when a potential is applied to the electrode with an ion-exchange membrane at the end regeneration process. In this case, some cations at the anode surface cannot be expelled, let alone be adsorbed by cathode. Fig. 10 (d) shows the transport of ions during the desorption process with the ion-exchange membrane. At the anode surface, the anions in the EDL could penetrate the anion-exchange membrane during the desorption process, but cations in the bulk solution were rejected by the anion-exchange membrane. Therefore, desalination efficiency was improved because of the selective transport of ions between the EDL and the aged electrode has a large bulk solution [6,27].

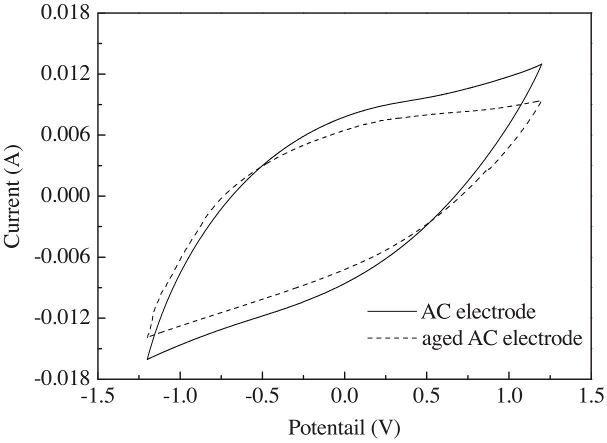


Fig. 9. Cyclic voltammograms of fresh electrode and aged electrode in 1 mol/L NaCl aqueous solution at a sweep rate of 10 mV/s.

Table 3
Surface functional groups of fresh electrode and aged electrode

Sample	–COOH (mmol/g)	–COOR (mmol/g)	–OH (mmol/g)	Total groups (mmol/g)
Fresh electrode	0.027	0.006	0.039	0.069
Aged electrode	0.391	0.197	0.011	0.599

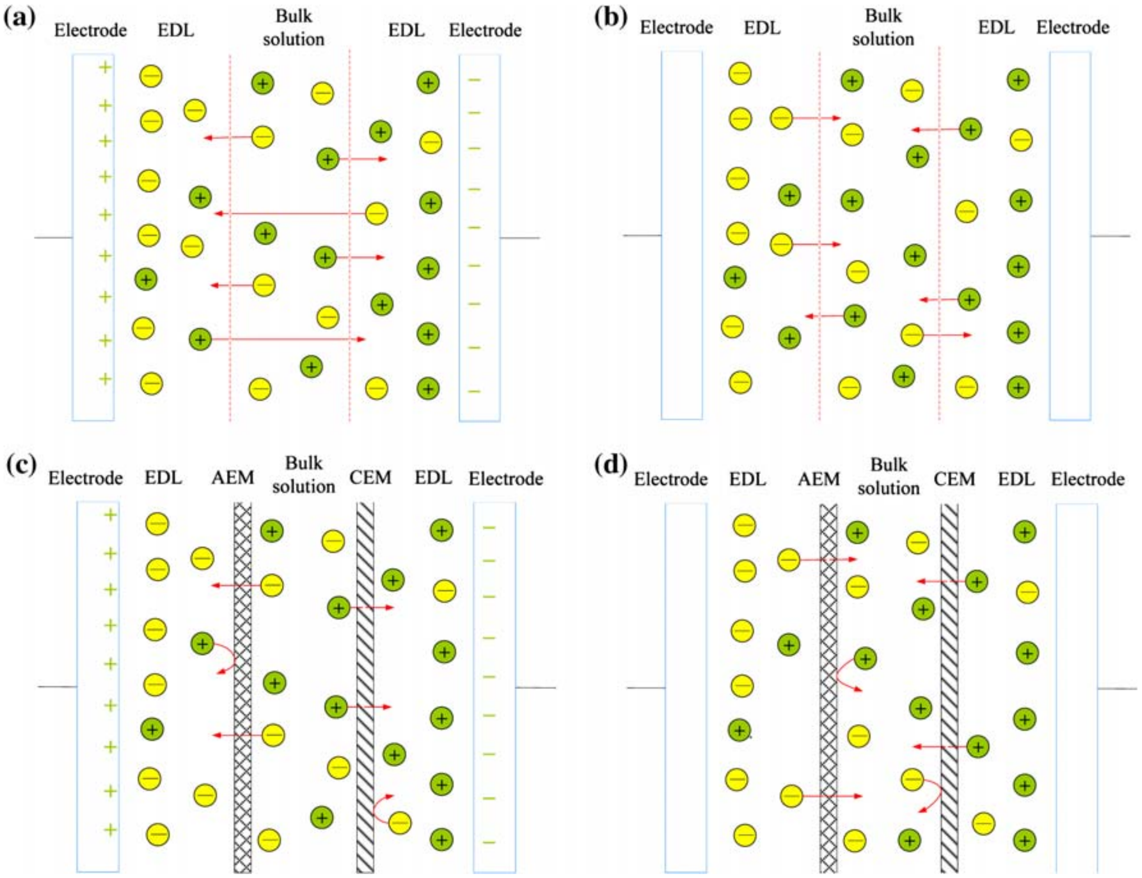


Fig. 10. The distribution and transport of ions at the electrode surface. Electrosorption mechanism without ion-exchange membrane (a), and desorption mechanism without ion-exchange membrane (b), and electrosorption mechanism with ion-exchange membrane (c), and desorption mechanism with ion-exchange membrane (d).

Because the aged electrode has a large amount of –COOH groups on the electrode surface, anion-exchange reaction will happen, as follows:

$$\text{–COOH} + \text{KCl} \rightleftharpoons \text{–COOK} + \text{HCl} \quad (6)$$

If an electrode has more –COOH groups, more K^+ will be accumulated on the electrode. When a potential was applied to the electrode, these K^+ at the anode surface were expelled and were immediately adsorbed by the cathode, as show in Fig. 10(a). This explains why the desalination efficiency of the aged electrode was much lower than that of the fresh electrode. However, if the anode surface is covered with an anion-exchange membrane, the K^+ cannot be expelled during the electrosorption process and moves to the EDL from the bulk solution during desorption. Again, this explains why the improvement in electrosorption with ion-exchange membrane was more significant with aged electrodes than with fresh electrodes.

4. Conclusions

The influence of aged AC electrodes and ion exchange membranes on desalination efficiency in electrosorption modules was investigated. Results indicated that microstructure changes occurred on the surface of aged electrodes. BET surface area of the aged electrode decreased to 753 from 828 m^2/g of the fresh electrode. The average pore size of the aged electrode increased to 2.28 from 2.26 nm of the fresh electrode. More surface functional groups, especially –COOH groups were formed on aged electrodes, and this caused the decrease of the electrosorption performance. With an initial concentration of 1,020 mg/L KCl and bias potential 1.5 V, the electrosorption capacity of aged electrodes decreased to 7.63 from 10.22 mg/g of fresh electrodes. The selective ion-exchange membrane can increase the electrosorption efficiency obviously, especially for aged electrodes.

References

[1] C.J. Gabelich, T. Tran, I.H.M. Suffet, Electrosorption of inorganic salts from aqueous solution using carbon aerogels, Environ. Sci. Technol. 36 (2002) 3010–3019.

[2] P. Bai, X. Chen, Y. Hang, J. Wang, G.H. Chen, A real trial of an innovative membrane bioreactor for saline sewage treatment, Desal. Water Treat. 18 (2010) 297–301.

[3] B.S. Oh, S.G. Oh, Y.J. Jung, Y.Y. Hwang, J.W. Kang, I.S. Kim, Evaluation of a seawater electrolysis process considering formation of free chlorine and perchlorate, Desal. Water Treat. 18 (2010) 245–250.

[4] D.Z. Martinez, E.C. Pozuelo, Project for the development of innovative solutions for the brines from desalination plants, Desal. Water Treat. 31 (2011) 206–217.

[5] T.-Y. Ying, K.-L. Yang, S. Yiacoumi, C. Tsouris, Electrosorption of ions from aqueous solutions by nanostructured carbon aerogel, J. Colloid Interface Sci. 250 (2002) 18–27.

[6] Y.-J. Kim, J.-H. Choi, Enhanced desalination efficiency in capacitive deionization with an ion-selective membrane, Sep. Purif. Technol. 71 (2010) 70–75.

[7] Y. Oren, Capacitive deionization (CDI) for desalination and water treatment—past, present and future (a review), Desalination 228 (2008) 10–29.

[8] H. Li, Y. Gao, L. Pan, Y. Zhang, Y. Chen, Z. Sun, Electrosorptive desalination by carbon nanotubes and nanofibres electrodes and ion-exchange membranes, Water Res. 42 (2008) 4923–4928.

[9] J.-A. Lim, N.-S. Park, J.-S. Park, J.-H. Choi, Fabrication and characterization of a porous carbon electrode for desalination of brackish water, Desalination 238 (2009) 37–42.

[10] Y. Gao, L. Pan, H.B. Li, Y. Zhang, Z. Zhang, Y. Chen, Z. Sun, Electrosorption behavior of cations with carbon nanotubes and carbon nanofibres composite film electrodes, Thin Solid Films 517 (2009) 1616–1619.

[11] S. Wang, D.Z. Wang, L.J. Ji, Q.M. Gong, Y.F. Zhu, J. Liang, Equilibrium and kinetic studies on the removal of NaCl from aqueous solutions by electrosorption on carbon nanotube electrodes, Sep. Purif. Technol. 58 (2007) 12–16.

[12] T.J. Welgemoeda, C.F. Schutte, Capacitive deionization technology™: An alternative desalination solution, Desalination 183 (2005) 327–340.

[13] L. Li, L. Zou, H. Song, G. Morris, Ordered mesoporous carbons synthesized by a modified sol–gel process for electrosorptive removal of sodium chloride, Carbon 47 (2009) 775–781.

[14] Z. Chen, C. Song, X. Sun, H. Guo, G. Zhu, Kinetic and isotherm studies on the electrosorption of NaCl from aqueous solutions by activated carbon electrodes, Desalination 267 (2011) 239–243.

[15] P.M. Biesheuvel, Thermodynamic cycle analysis for capacitive deionization, J. Colloid Interface Sci. 332 (2009) 258–264.

[16] E. Avraham, M. Noked, Y. Bouhadana, A. Soffer, D. Aurbach, Limitations of charge efficiency in capacitive deionization processes III: The behavior of surface oxidized activated carbon electrodes, Electrochim. Acta 56 (2010) 441–447.

[17] M. Zhu, C.J. Weber, Y. Yang, M. Konuma, U. Starke, K. Kern, A.M. Bittner, Chemical and electrochemical ageing of carbon materials used in supercapacitor electrodes, Carbon 46 (2008) 1829–1840.

[18] R. Berenguer, J.P. Marco-Lozar, C. Quijada, D. Cazorla-Amorós, E. Morallnó, A comparison between oxidation of activated carbon by electrochemical and chemical treatments, Carbon 50 (2012) 1123–1134.

[19] M.J. Bleda-Martínez, D. Lozano-Castelló, E. Morallón, D. Cazorla-Amorós, A. Linares-Solano, Chemical and electrochemical characterization of porous carbon materials, Carbon 44 (2006) 2642–2651.

[20] A.G. Pandolfo, A.F. Hollenkamp, Carbon properties and their role in supercapacitors, J. Power Sources 157 (2006) 11–27.

[21] M. Andelman, Flow through capacitor basics, Sep. Purif. Technol. 80 (2011) 262–269.

[22] M. Andelman, G.S. Walker, Patent US 6709560 Charge Barrier Flow Through Capacitor, 2000.

[23] H.P. Boehm, Some aspects of the surface chemistry of carbon black and other carbons, Carbon 32 (1994) 759–769.

[24] E. Bayram, E. Ayranci, A systematic study on the changes in properties of an activated carbon cloth upon polarization, Electrochim. Acta 56 (2011) 2184–2189.

[25] R. Berenguer, J.P. Marco-Lozar, C. Quijada, D. Cazorla-Amorós, E. Morallón, Effect of electrochemical treatments on the surface chemistry of activated carbon, Carbon 47 (2009) 1018–1027.

[26] C.O. Ania, F. Beguin, Mechanism of adsorption and electrosorption of bentazone on activated carbon cloth in aqueous solutions, Water Res. 41 (2007) 3372–3380.

[27] J.Y. Lee, S.J. Seo, S.H. Yun, S.H. Moon, Preparation of ion exchanger layered electrodes for advanced membrane capacitive deionization (MCDI), Water Res. 21 (2011) 5375–5380.