Int. J. Electrochem. Sci., 8 **(2013)** 4864 - 4872

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

The Study of Modified PAN-based Carbon Fiber Felt as Electrode in the Electro-adsorption Desalination

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Received: 1 February 2013 / *Accepted:* 12 March 2013 / *Published:* 1 April 2013

Cooling circulating water drainage from Jun Zheng Plant has been disposed with a kind of electrode material of high capacitive properties----PAN-based Carbon Fiber Felt. Meanwhile, chemical oxidation and heat treatment have been used to modify this carbon fiber felt and the properties of Electro-adsorption Desalination have been researched respectively. With the increase of voltage, the conductivity of outlets decreases a lot, especially under the modified electrode; while with the rise of time, adsorbance in chemical oxidized electrodes has been larger than that in heat treated ones, although which adsorb organic pollutants much greater.

Keywords: Electro-adsorption; PAN-based Carbon Fiber Felt; modified

1. INTRODUCTION

The phenomenon of enterprises' sewage discharge has been worse and worse with the growth of industry. In order to save the cost of production and achieve sustainable development, putting "energy-saving and emission-reduction" into effect has been necessary so that the waste water can be reused. Presently, researchers generally adopt activated carbon with high area as electrode materials. However, under the limitation of small effective surface area, poor conductivity and desalinating in low concentration [1-3]. Seeking for a certain electrode materials with better conductivity, higher strength, more aperture gap, bigger effective surface area, more favorable stability and longer cycle has become the first priority.

Carbon Fiber Felt has the advantages of heat resistance, fine mechanical strength, large surface area and high conductivity. The electrodes in this experiment adopted PAN –based Carbon Fiber Felt with the weight of 500g/m^2, longitudinal and transverse strength (N/mm^2) of 0.12,0.16, elongation at

break of 3%, 4%, resistivity ((Ω•m)of 4~6, surface area of over 1.5m^2/g, which is considered to be a sort of favorable sorbing material[4-6].

Modification was used in PAN –based Carbon Fiber Felt electrodes, and we studied the electro-adsorption desalination effect under different conditions respectively.

2. EXPERIMENTAL PART

2.1 Materials and Instruments

PAN –based Carbon Fiber Felt: Shanghai Ai Ji Carbon Co.,Ltd. (Thermal conductivity: 0.06W/(m•K)(298K); fixed carbon: >94%; sulfur content: <0.03%) 202-1 Electrically Heated Drying Oven; Manmade Electro-adsorption Vessel(cm): 100×40×40; Conductivity Meter AP-2 HM: Xuzhou Ya Ming Appliances Co.,Ltd.; LZB Glass Rotameter; Filter: Beijing Heng Zhu Technology Co.,Ltd; Piezometer SKON: Taiwan Xie Gang; DC Power Supply: 0-15 V, 0-2 A adjustable.

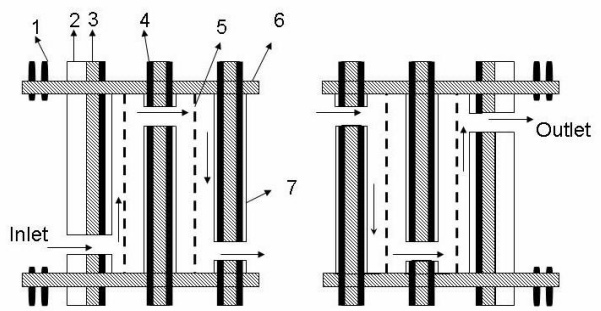
2.2 The modification of PAN –based Carbon Fiber Felt

1) Chemical oxidized surface modification: put PAN –based Carbon Fiber Felt into the HNO_3 solution for 1h, then washed to be neutral with distilled water, dried in vacuum at 393K for 5h, aside.

2) Heat treated surface modification: dealt with PAN –based Carbon Fiber Felt at 333-2273K，kept in N_2 at constant temperature for 1h, then cooled naturally.

2.3 Electro-adsorption Experiment process

This Electro-adsorption Experiment module adopted EMK110, which has the electrodes of 400 mm×200 mm×2 mm (length×width×thickness). Put 50 pairs of electrodes together (plate spacing about 6 mm) into a module with the size of 350 mm×220 mm×460 mm (length×width×height). Then made two modules in series to shorten regeneration time and enhance efficiency, as shown in Fig.1.



1. Nut; 2. End sheet; 3. Board; 4. Conducting layer; 5. Grid; 6. Screw bolt; 7. Electrode

Figure 1. Electro-adsorption modules in series

The process route is shown in Fig.2: circulating cooling water came through the pretreatment of Multi Media Filter into the water tank which can be designed in terms of practical need, then entered electro-adsorption module by centrifugal pump after filling with water tank, finally treated water with low inorganic salt could be gathered in the production tank. When primary treatment can meet the requirements, middle water tank can be fixed to make the produced water store temporarily for repeated treatments. The parameters of the raw water can be seen in Table1.

Table 1. the parameters of the raw water

conductivity	COD	Chloride concentration	pH	suspended solids
1750μS/cm	>5mg/L	270~300 mg/L	6.1	<5

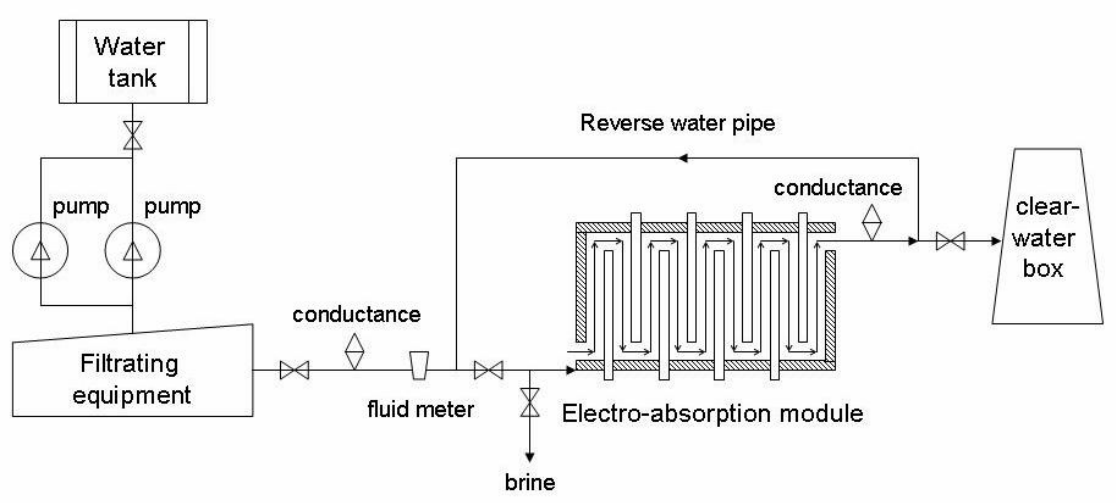


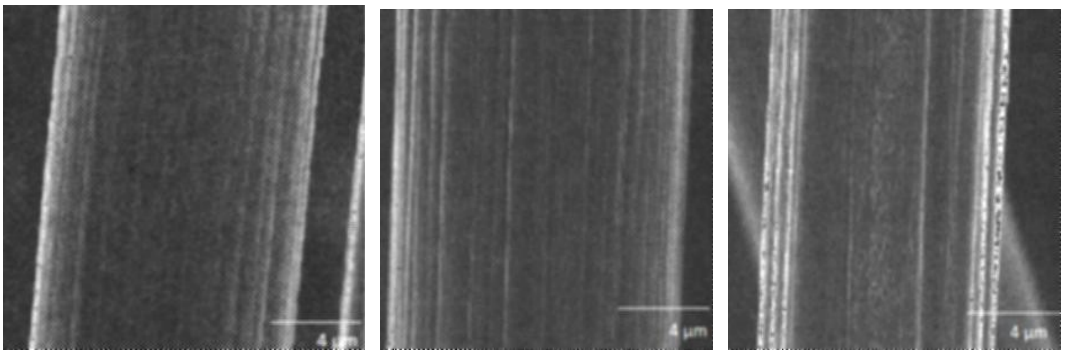
Figure 2. The process route of dealing with raw water

3. RESULT AND DISCUSSION

3.1 Characterization of modified PAN-based Carbon Fiber Felt

From the result of SEM (Fig.3), we can see that, before the treatment, on the surface of PAN-based Carbon Fiber Felt there were narrow and shallow axial ditches which would be wider and deeper obviously after chemical oxidized treatment. However, after heat treatment, there appeared several small potholes and bands on the surface of PAN-based Carbon Fiber Felt. It means that directed or ordered degree of numerous aromatic molecular planes contained by carbon felt has improved remarkably, from amorphous or disordered graphite structure into ordered graphite structure. According to Donnet J. B.[7], the performance of fiber reinforced composites mainly depends on the interface performance between reinforced fibers and matrix materials, while such performance can be

affected by mechanical friction which is related with fiber specific surface area and surface morphology as well as chemical bond force which is related with chemical activity between fiber and matrix. So the treatment of fiber surface can firstly prevent the appearance of weak interface layer which includes impurities and release agents adsorbed during production process, the oxide and hydrate layers formed during interface aging and the air layer confined during the inadequate infiltration with matrix. Secondly, the carbon layers initially linked weakly can be removed; micropores and etching trenches can be formed on the surface, which makes the specific area increase. What's more, polar or reactive groups can be introduced on to the fiber surface, which can enhance surface activity, increase the chemical bond force between fiber and matrix. Thereby the adsorption ability can be enhanced.

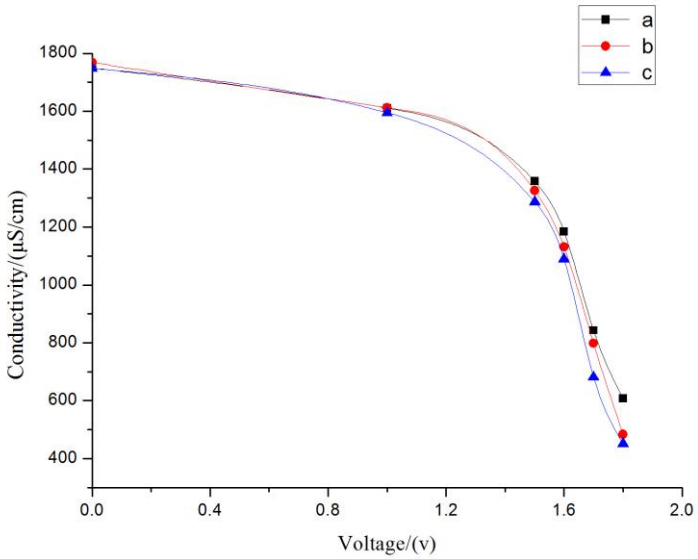


(a) Untreated PAN-based carbon fiber; (b) chemical oxidized PAN-based carbon fiber; (c) heat treated PAN-based carbon fiber

Figure 3. the SEM of PAN-based carbon fiber

3.2 The impact of voltage on Electro-adsorption desalination with PAN-based carbon fiber felt as electrodes

The value of conductivity can stand for the total salt content in the water, so we can use the decrease of conductivity as the effect of dechloridation. Under untreated and two-kind modified electrode materials, the outlets' conductivities within 40 min were measured with the voltage of 1.5 V, 1.6 V, 1.7 V, 1.8 V. The result can be seen in Fig.4. Z. Li [8] also did such kind of experiment using carbon gel as electrode material; the result showed the desalination effect would be better when the influent concentration was lower. However, when the influent concentration is higher, our carbon fiber felt electrode has more efficient desalination effect. It means that, when influent concentration is low, the size of apertures play an important role in desalination while, when influent concentration is high, the specific area takes control. When using ordinary activated carbon as electrode, polymer binder will be used to bind them together. But such binder will be adsorbed on to the carbon surface, which will increase transfer resistance of current and solute. Besides, the contact between them is not so tight that higher resistance will be produced, so there has been a long way to go before practical application. Comparing with that, carbon fiber felt improves the weakness. It makes adsorption steady and rapid.



(a) Untreated PAN-based carbon fiber felt; (b) chemical oxidized PAN-based carbon fiber felt; (c) heat treated PAN-based carbon fiber felt

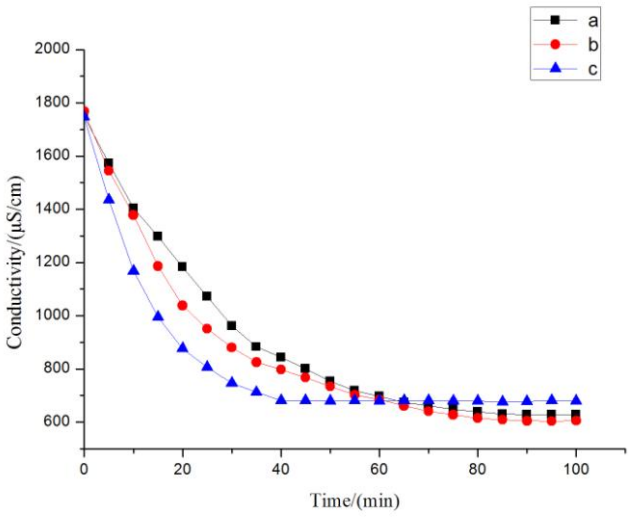
Figure 4. the outlets' conductivities within 40 min under different voltages

From above, it is demonstrated that the conductivity descended as the voltage went up. When the voltage reached as high as 1.8V, there appeared a few bubbles in the produced water, indicating that hydrolysis had happened and the loss of module energy would be increased, therefore, the voltage should be confined within 1.7V. Besides, the adsorptivity of modified PAN-based carbon fiber felt electrodes was much higher than that of untreated ones. Because there were more micro voids in the acid oxidized carbon felt which then conducted electricity more easily; after heat treated, the degree of graphitization had enhanced a great deal, which result in the decrease of resistivity, so the conductivity enhanced as well.

3.3 The impact of adsorbing time on Electro-adsorption desalination with PAN-based carbon fiber felt as electrodes

Under the voltage of 1.7V, we measured the connection between changes of time and conductivities. Fig.5 shows that the conductivity fell sharply within the first 40min, and then became steady. The adsorptivity of chemical oxidized carbon felt electrodes appeared higher than that of untreated ones while heat treated ones appeared lower. It has been analyzed that, after being oxidized, carbon felt electrodes were provided with more oxygen-containing functional groups of the C-OH,-COOH, and C=O, so the infiltration properties of carbon felt surface have risen considerably[9]. Due to the corrosive effect of acid, the specific surface area of oxidized carbon felt became much larger than that of untreated one. High heat treatment improved the ordered arrangement degree of graphite structure, which not only reduced the superficial area of the electrodes, but lessen the surface content of hydrophilic oxygen-containing functional groups as well. As a result, the surface of carbon felt

couldn't infiltrate favorably with solution, and effective active center reduced, and electrochemistry activity of the electrodes decreased.

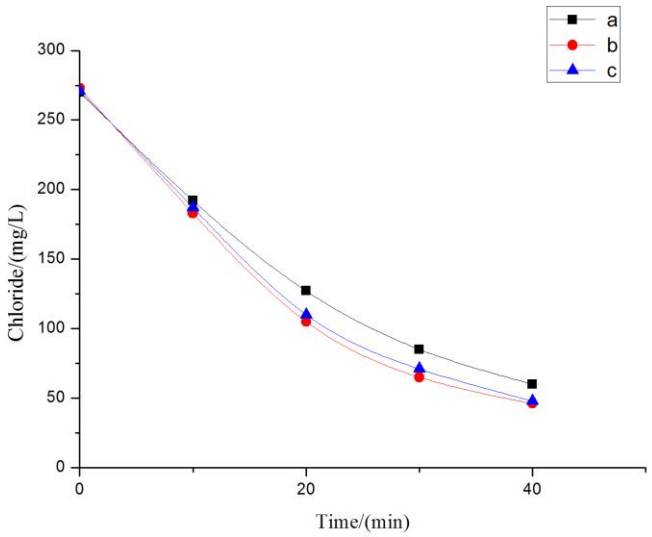


(a) Untreated PAN-based carbon fiber felt; (b) chemical oxidized PAN-based carbon fiber felt; (c) heat treated PAN-based carbon fiber felt

Figure 5. the outlets' conductivities under 1.7V within different times

3.4 The effect of electrodes on removal of chloride

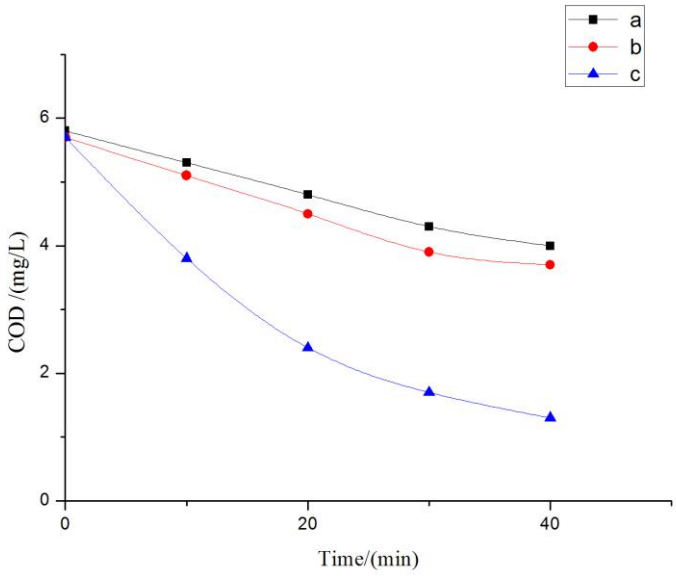
On the condition of 1.7V, 40min, it is observed that the adsorption to chloride of modified carbon felt electrodes was higher than that of untreated ones. Electro-adsorption is dynamic balance movement of irons in electric field, and the directed movements of chloride is more active than that of other particles, so the adsorption proportion is relatively higher when electrodes have better electroconductivity. As shown in Fig.6. S. Sun, et al. [10] studied the electric adsorption properties in chloride solution by adopting activated carbon electrode. The result showed, though they used activated carbon with high specific surface area---the size of apertures were so small---"overlapping" adversely affects the production of electric double layer[11]. The adsorption rate was low relatively. Comparing with that, carbon fiber felt has abundant microporous with narrow distribution---especially modified carbon fiber can be contacted with adsorbates more easily, and small diffusion resistance. So to some extent, the adsorption and desorption rate are higher, which is benefit for adsorbing and separating.



(a) Untreated PAN-based carbon fiber felt; (b) chemical oxidized PAN-based carbon fiber felt; (c) heat treated PAN-based carbon fiber felt

Figure 6. The effect on removal of chloride

3.5 The effect of electrodes on removal of organic pollutant



(a) Untreated PAN-based carbon fiber felt; (b) chemical oxidized PAN-based carbon fiber felt; (c) heat treated PAN-based carbon fiber felt

Figure 7. The effect of electrodes on removal of organic pollutant

On the condition of 1.7V, 40min, we conclude from Fig.7 that the COD in heat treated carbon felt electrodes declined more. It is analyzed that, after heat treatment on PAN, parts of nitrile grouping (-C≡〖KG-*5/7〗≡N) changed into diglycolamidic(-C=〖KG-*4/7〗= N), and chain structure

changed into ring structure, π electrons in MWNTs became strong π-π conjugate with thoset in modified PAN[12], so the adsorption to organic ingredients boost up. Generally speaking, it is easy to use polarization to enhance adsorption. However, the reversibility of electric adsorption can be confined by practical application system, particularly in several systems with strong specific adsorption. Electric desorption is usually part of electrostatic adsorption while other parts are affected little, even the situation of adsorption not changing with current or voltage will appear. We can see that apparently in organic adsorption. As we know the reversibility of inorganic ions adsorption is better than that of organic ones, so we can make carbon fiber electrochemical oxide in order that the pollutants oxidative degrade while PCF (PAN-based Carbon Fiber) will be reborn or changed into other valuable products. In a word, comparing with other carbon fiber electrode, MPCF not only has the advantages of adsorbing inorganic ions, but is also good at adsorbing organics. It means MPCF will be a good choice in the future if considering comprehensively the electrode material adsorption performances.

4. CONCLUSION

(1) This experiment adopted EMK110 adsorption module and PAN-based Carbon Fiber Felt as electrodes, reached a conclusion that the outlets' conductivities decreased with the increase of voltages which means the adsorptivity enhanced. Modified PAN-based Carbon Fiber Felt electrodes were more sensitive to the changes of voltage because of their higher electrical conductivity.

(2) With the raise of adsorbing time, the outlets' conductivities went down, obviously within the first 40min, and then became steady. When using chemical oxidized PAN-based Carbon Fiber Felt electrodes, adsorptivity enhanced due to the amplification of specific surface area of carbon felt, and infiltration properties improved a lot. When adopting heat treated AN-based Carbon Fiber Felt electrodes, adsorptivity decreased, that was because the specific surface area reduced, consequently made the electrochemistry activity of electrodes decline.

(3) Modified electrodes can strengthen the adsorption to chlorides, especially heat treated PAN-based Carbon Fiber Felt electrodes can obviously reduce the content of organic ingredients, indicating that the structure of electrodes are al so a main reason for affecting adsorption, there should be a certain relationship between structure of matter and electro-adsorption.

ACKNOWLEDGEMENT
The research was supported by EST Co.,Ltd.

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