Study on the Treatment of Circulating Water: PPy/PAN-based Activated Carbon Fiber Felt Composite as Electro-adsorption Electrode

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Abstract: This study adopted PPy/PAN-based carbon fiber felt composite as a new electrode for desalination experiment. The result shows that this kind of composite electrode can significantly reduce the outlet conductivity when inlet chemical oxygen demand (COD) is over 300 mg/l. It additionally reduces COD to the value obtained with other electrodes.

Keywords: COD, absorption, polypyrrole, desalination, conductivity

1. INTRODUCTION

Products and processing objects in various sectors will cause the differences in wastewater composition, which requires flexibility in industrial wastewater desalination. For the power plant, there remains not only inorganic salt in the outlet, but a small amount of organics, suspended solids, antisludging agent and ash as well; however, its water quality is not as low as that from chemicals and textile printing and dyeing enterprises [1-2]. If the same desalination method is adopted, extra costs will be caused; therefore, economical and scientific desalination process should be studied [3].

At present, there is mainly electric adsorption and reverse osmosis membrane for industrial wastewater desalination. The former has the advantages of lower components costs, energy- saving and lower water quality requirements. For example, its inlet COD should be no more than 150 mg/l while the latter's inlet COD less than 40 mg/l [4-5]. In power plant, wastewater COD is below 300 mg/l via cartridge filter; it is only operative to handle inlet with COD over 300 mg/l by using reverse osmosis and ultrafiltration membranes together (double membranes). However, in case the wastewater COD reaches 2000~15000 mg/l in several highpolluting enterprises, both electric adsorption and double membranes need complicated pretreatment to reduce COD to inlet standard [6-9]. In order to reduce operating cost, the core elements in electric adsorption need improving to realize high desalination efficiency and COD reduction when inlet COD is up to 300 mg/l.

The key point in electric adsorption is the choice of electrode materials. Now a days, there mainly includes carbon fiber, carbon nanotubes and related composites. Metal plates are covered with such materials, set up positive and negative DC voltage respectively and contact with wastewater directly. Ions in the water migrate to electrodes and gather there, and then double layer is formed in the inner side of each plate. Hydroxyl radicals (OH) with strong oxidation are generated on this occasion, which enable parts of

Mesoporous electrode material

Microporous electrode material

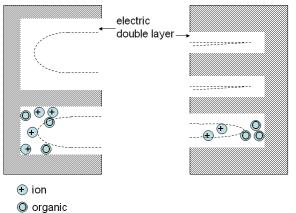


Figure 1. pore diameter influences the electric double layer.

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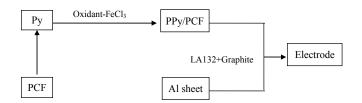


Figure 2. the preparation of PPy/PCF composite.

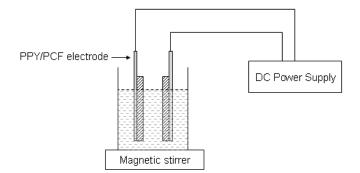


Figure 3. Electric adsorption desalination device.

organics to degrade to reduce COD. In practical work process, pores in electrode materials make the surface area of double layer much larger than the flow area of the longitudinal channel, which increases the opportunity to adsorb charged ions; moreover, several organic suspended matters and inhibitors may be attached to the holes due to the porous structure. It means that desalination can affected by electric double layer overlap and physisorption of organic particles in micro porous material, as shown in Fig.1.

Activated carbon fiber felt and carbon nanotubes are unfavourable for inlet with COD over 150mg/l. As too many organic particles occupy the channel because of physical adsorption, which affects desalination efficiency and pollutes components. Better results have been achieved by adopting Carbon Nanotubes/PAN-based Carbon Fiber Felt (CNT/PCF) as electrode, but the stain resistance still needs to be improved because of the special pore structure of carbon nanotubes [10-13].

As a common conductive polymer, polypyrrole (PPy) has a surface area of 3000m²/g, and more mesopores structure (about 100 nm), which is benefit for adsorption process. But primary bond of PPy is likely to break during charging and discharging process, which will negates the effects of material, and PPy monomer is not easy to store [14], so we prepare a kind of stable composite by PPy and PAN-based Activated Carbon Fiber Felt.

2. EXPERIMENT

2.1. Materials

Py: CP, Sinopharm Chemical Reagent Co., Ltd.; SDS: AR, Vicente Biotechnology (Nanjing) Co., Ltd.; FeCl₃: AR, Heyzer Mei Industrial Co., Ltd.; LA123: Beijing solid Qin Bo Yuan Technology Co., Ltd.; PCF: Nantong Sen You Carbon Fiber Co., Ltd.; 85-2 thermostat magnetic stirrer: Jintan Ronghua Instrument Manufacturing Co., Ltd.; DZF-2001B vacuum oven: Shanghai Yi Heng

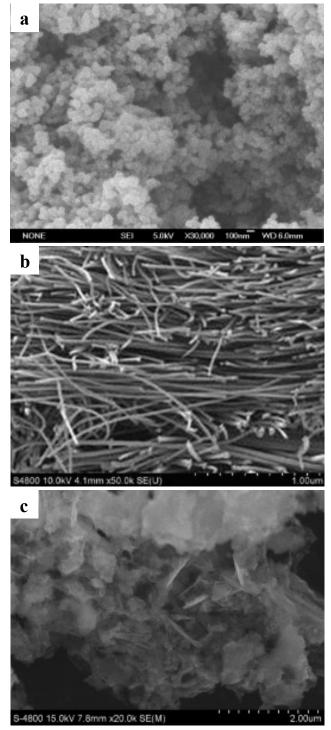


Figure 4. a. SEM image of PPy; b. SEM image of PCF; Fig. 4c SEM image of PPy/PCF.

Scientific Instrument Co., Ltd.; GZP(K)730 tabletting machine: Shanghai Tianhe Pharmaceutical Machinery Co., Ltd.

2.2. Preparation of PPy/PCF

Put PCF slice into moderate pyrrole at the room temperature,

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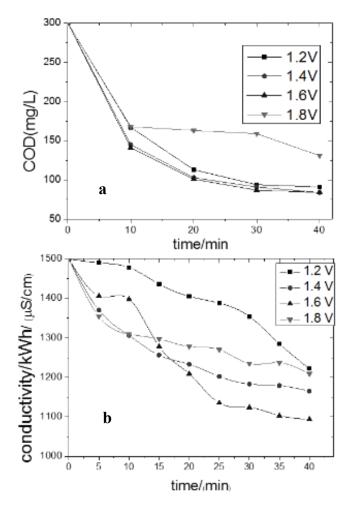


Figure 5. a. COD rates at different voltages; b. Conductivities rates at different voltages.

adsorbed for half an hour then took out; placed for an hour and then immersed into $FeCl_3$ solution. After in-situ polymerization, black PPy will be synthesized on the PCF surface; reacted for half an hour, took out and washed by distilled water for 3 times, flattened and dried. By adopting a small amount of graphite as a conductive agent, water-soluble polymer LA132 as binder, adhered sample to Al sheet to obtain the test electrode, as shown in Fig.2.

Desalination performance testing process can be seen in Fig.3: including an adjustable DC power supply, a pair of PPy / PCF composite electrode and temperature magnetic stirrer. Test water imitates power plant recirculated cooling water: conductivity of 1500 μ S/cm, chloride content of 580 mg/L. Put 0.12g HOOCC₆H₄COOK into 1000ml NaCl solution, got COD value of about 150 mg/l, accordingly prepared 200 mg/l, 300 mg/l, 400 mg/l and 500 mg/l respectively.

3. RESULT AND DISCUSSION

3.1. Morphology Analysis of PPy/PCF composites

From the Fig.4a, we can see that PPy has a porous structure with the diameter of about 100 nm. PCF has a three-dimensional network structure (Fig.4b). To some extent, the fibers act as frame-

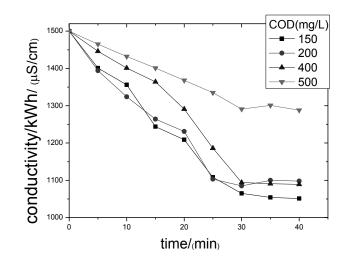


Figure 6. Conductivity changes at inlet COD of 150 mg/l, 200 mg/l, 400 mg/l and 500 mg/l.

work which has good mechanical strength and stability. PPy/PCF composites (Fig. 4c) contain more particles which scatter in a 3D space, more linkers connecting and supporting and a plurality of pores which can provide multi low paths through the liquid substance, filter and separate suspended natters, large shaped substances and so on.

3.2. Choice of Working Voltage under PPy/PCF Composite Electrodes

Five water samples (COD: 300mg/l; conductivity:1500 µS/cm;) were prepared, and the experimental voltages were arranged as 1.2 V, 1.4 V, 1.6 V, 1.8 V. During the working time of 40 min, outlet conductivity was measured every 5 min, and COD of outlet was measured every 10 min. As shown in Fig.5, COD measured is less than 100 mg/l after 30 min, which meets discharge standard. From Fig.5b, we can see the effect of voltage on desalination. Outlet conductivity decreases with time and stabilizes at 25~30 min. 1.6 V is the best choice, as at 1.8 V, hydrolysis starts and electrodes have part of energy lose when charging. The similar condition occurs when inlet CODs are 150 mg/l, 200 mg/l and 400 mg/l, as shown in Fig.6. When inlet COD is 500 mg/l, the desalination effect declines: COD removal rate increase while conductivity decline becomes worse, which can be controlled below 1300 µS/cm, however. It means that this kind of electrode can desalinate fluently when ensuring the decrease of COD and 1.6 V is the best choice.

3.3. Comparison of Different Electrode Materials

PCF, nanotube and PPy/PCF were adopted respectively as electrodes. The working voltages were arranged as 1.6 V and inlet conductivity was 1500 μ S/cm. During the working time of 30 min, COD and conductivity of outlet were recorded and compared, as shown in Fig.7.

When the COD is low, nanotube has better desalination. Because its hollow microporous structure has better conductivity. But its desalting ability decreases with the increase of the COD, as organic particles enter into micropores during COD degradation process [15]. This physical adsorption affects the capacity of the electric - PPY/PCF

Nanotube PCF

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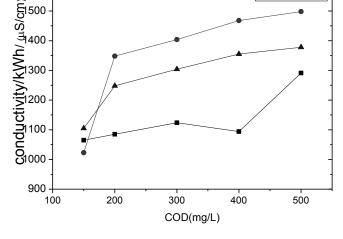


Figure 7. Conductivities and COD rates under different electrode materials.

double layer, part of which overlaps because of the narrow space, so ions are not able to stay there. PCF has better stability. When the COD is 300 mg/l, the conductivity decreases to 1300 μ S/cm. Considering its low cost, it can be applied in primary drainage or some occasions which has low demands for outlet. PPy/PCF adsorbs organic particles in its pores; meanwhile, there is enough space for Cl⁻ to stay. So it can also work well after the electric double layer has been set up.

Fig.8 shows the outlet water conductivity of three kinds of materials when the COD rate is 150 mg/l, the working time is 20 min. We can see that at 1.4 V, PPy/PCF composite electrode exhibits the lowest conductivity, as the proper aperture is benefit for the adsorption of electric double layer on the micro interface. To make energy saving, the voltage of the working electrode of the process should be set at 1.4 V.

4. CONCLUSION

- PPy/PCF composite electrode can ensure desalination efficiency when inlet COD is over 300 mg/l, which has advantages of lowering cost and simplifying pretreatment devices;
- 2) When circulating water from power plant has initial conductivity of 1500 μ S/cm, PPy/PCF composite electrode enhances both desalting ability and COD removal ability with the increase of working voltage. The optimum operating voltage is 1.6 V. Compared with nanotube and PCF electrodes, PPy/PCF composite can reduce working voltage to 1.4 V to save energy.

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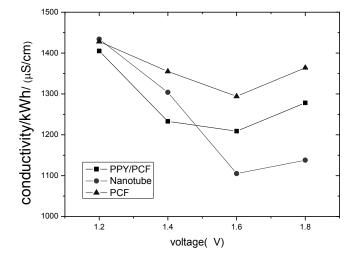


Figure 8. Conductivities of three Materials at different Voltage.

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