Membrane Water Treatment, *Vol. 5*, *No. 1* (*2014*) *31-40*
DOI: http://dx.doi.org/10.12989/mwt.2014.5.1.031

Improving the smoking quality of papermaking tobacco sheet extract by using electrodialysis

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(*Received December 06*, *2013*, *Revised January 08*, *2014*, *Accepted January 09*, *2014*)

Abstract. Papermaking tobacco sheet is an important reclaimed process for cigarette making. Traditionally, the pressure driven membrane was often used to isolate the effective compounds from the tobacco sheet extract. However, this method is difficult to remove small ionic compounds. Besides, membrane fouling is a major problem for effective use of these pressure driven membrane technologies. In this study, the electrodialysis process is used to removal the chloride ions and nitrate ions, thus the smoking quality of papermaking tobacco sheet extract can get improved. Three types of electrolytes (Na_2SO_4, NaCl and HCl) are chosen to prevent the generation of precipitation. The results indicate that 0.1 mol/L HCl at current density of 30 mA/cm^2 is the optimal condition for the electrodialysis process. The removal rates of the Cl^- and NO_3^- in tobacco sheet extract are 97% and 98.4%, respectively. The electrodialysis process cost was estimated to be 0.11 $/L. Naturally, electrodialysis is not only technological feasible, environmental-friendly and economical-attractive for tobacco extract treatment.

Keywords: papermaking tobacco sheet; tobacco extract; electrodialysis; ion-exchange membranes

1. Introduction

Reconstituted tobacco or tobacco sheet has been used widely in the tobacco industry for its advantageous economic impact on the manufacturing cost of cigars and cigarettes (Wang *et al.* 2005). There are three usual methods for preparation of tobacco sheet: rolled tobacco sheet, slurry processed tobacco sheet and papermaking tobacco sheet. Among them, papermaking tobacco sheet has incomparable superiority in structural strength, combustion performance and tar delivery. However, the publications (Wang *et al.* 2011, Baker *et al.* 2004, Zenzen *et al.* 2012, Zhou *et al.* 2013) are considered that the papermaking tobacco sheet is still in the infant stage of development in China, with many disadvantages such as high energy consumption, low yield efficiency and poor quality. So, more researches in papermaking process tobacco sheet need to be done.

In present, tobacco sheet extracts are treatment of microfiltration or nanofiltration methods to remove the proteins, pectin and other macromolecules. However, some small molecular ions like

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http://www.techno-press.org/?journal=mwt&subpage=7 ISSN: 2005-8624 (Print), 2092-7037 (Online)

chloride and nitrate ions are unable to be removed through the pressure membranes. Johnson *et al*. (2009) have described that these ions have significant influence on the quality and taste of the smoke. The publications (Müller *et al*. 2011, Zarrelli *et al*. 2012) indicated that chloride ion is an essential mineral element in flue-cured tobacco, which will affect the quality indexes of flue-cured tobacco, such as moisture absorptivity, combustibility. Meanwhile, nitrate ion is one of the most harmful element for human health since nitrate ion can react with alkaloids and form tobacco-specific nitrosamines during tobacco burning (Seyler *et al*. 2013, Narkowicz *et al*. 2013, Nunes-Alves *et al*. 2013). In China, the Technical Standard System of Tobacco and Tobacco Product suggests the chloride and nitrate ions concentration should not be higher than 0.8% (w/w) and 0.5% (w/w), respectively. Therefore, it is necessary to minimize the chloride and nitrate ions during the preparation of papermaking tobacco sheet.

Electrodialysis is a novel separation technology, which has found more and more significant applications in chemical cleaner production, environmental protection and energy conversion. Electrodialysis has the advantages of low energy consumption, high efficiency, continuously running and friendly to environment etc. (Huang *et al*. 2007). Due to the permselectivity characteristic of ion exchange membranes, the cations can be transported across the cation exchange membranes and be retarded by the anion exchange membranes under an applied of electric field. Based on the principle of electrodialysis process, this technology can be used to remove the undesired chloride and nitrate ions in the papermaking tobacco sheet extract. At the same time, the active ingredients like proteins, pectin and sugars cannot be hydrolyzed, so they are retained. Since the components of tobacco extract are very complex, including nicotine, proteins, alkali metals, alkaline earth metals, anions, sugars, pigments, amino acids, etc. In electrodialysis process, the metal ions can react with some electrolyte anions or hydroxyl ions caused by concentration polarization in charged membranes that could induce fouling of the ion exchange membranes. Therefore, it is necessary to monitor the electrodialysis process and take some pretreatment or post-treatment measures to eliminate the fouling of the membrane. The main objectives of this study are: (1) to test feasibility of the electrodialysis technology for the removal of undesired chloride and nitrate ions in tobacco sheet extract; (2) to identify the most suitable electrolytes; (3) to estimate the process of electrodialysis for tobacco sheet desalination.

2. Statistics on seawater desalination

2.1 Pretreatment

Tobacco extract (solid content ~ 40%) used in this experiment is obtained from China Tobacco Anhui Industrial CO., Ltd, Hefei, Anhui Province, China. There are some suspended solids in the tobacco solution. A pretreatment process is needed to meet the requirement for electrodialysis operation. The ceramic membrane module (Hefei ChemJoy polymers Materials CO., Ltd, China) with a pore size of 50nm is used to remove the above suspended solids (Zhong *et al*. 2013).

2.2 Apparatus

The laboratory-scale experimental equipment was mainly comprised of four parts: (a) Direct current power supply (WYL-605 × 2S,Hangzhou Yuhang Si-ling Co.LTD., China); (b) Beakers to store the feed; (c) Immiscible pumps (HJ-311, Zhejiang SenSen Co.LTD., China) to circulate the solution at the maximal speed of 300 L/h; (d) Electrodialysis stacks.

The A (anion-exchange membrane)-C (cation exchange membrane) configuration with one repeating unit was applied in these experiments to desalination (Fig. 1). Specifically, the stack has (a) a cathode and anode, which are made of titanium coated with ruthenium; (b) Plexiglas spacers (thickness = 0.3 mm) to separate the membranes with Viton gaskets as the seals; (c) a cation exchange membrane (JCM-II-07, Beijing TingRun Membrane, China), an anion exchange membrane (JAM-II-07, Beijing TingRun Membrane, China), all with an effective membrane area of 100 cm^2 and their properties are listed in Table 1; (d) supporting electrolyte solutions and electrode rinsing solutions, which were both prepared from sodium sulfate.

All the experiments were conducted at a constant current density of 30 mA/cm^2. A Na_2SO_4 solution (0.3 mol/L, 400 mL) was used as the electrode rinsing solution. The concentrated chamber was fed with three kinds of electrolytes, i.e., Na_2SO_4, NaCl, HCl (0.1 M, 400 mL). The diluted chamber was fed with pretreated tobacco extraction (400 mL). All chemicals were of analytical grade and used as received. Distilled water was used throughout experiment.

2.3 Desaliantion rate and energy comsumption

Desalination rate (Dr) was calculated as Eq. (1)

Table 1 Some commercial UF membranes with pore size between 0.01 and 0.02 μm

	Membranes	Thickness (μm)	IEC (mmol/g)	Water ratio (%)	Resistance ($\Omega\cdot cm^2$)	Transport number (%)
AEM	JAM-II-07	160-230	1.8-2.2	24-30	4-8	90-95
CEM	JCM-II-07	160-230	2.0-2.9	35-43	4-8	90-95

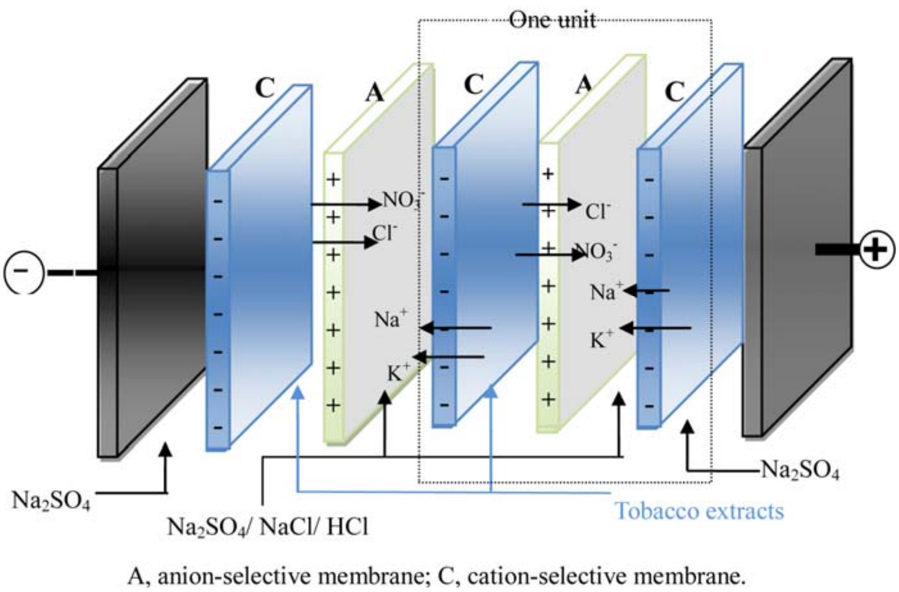

Fig. 1 Schematic of the ED stack used for experiments

$$D_r = \frac{\kappa_a}{\kappa_b} \quad (1)$$

κ_b and κ_a are the conductivity of tobacco extracts at time 0 and t, respectively. The energy consumption E (kW·h/L) was calculated as Eq. (2).

$$E = \frac{\int_0^t UIdt}{V} \quad (2)$$

Where U is the voltage drop across the ED stack (V), and I is the electric current (A), V is the volume of tobacco extract (L).

2.4 Analytical methods

The solution in the feed and concentrate chamber was diluted for 100 times and conductivity of the feed solution was monitored with a conductivity meter. (DDS-307, Inesa Analytical Instrument Co., LtD. Shanghai LeiCi, China). The concentration of chloride ions (Cl^-) and nitrate ions (NO_3^-) were determined by Ion Chromatography (ICS3000 multifunctional ion chromatography and ED electrochemical detector, DIONEX Company, USA).

3. Results and discussion

3.1 Pretreatment process

Ceramic membrane with a pore size of 50 nm is used for pretreatment of tobacco extract (0.15 MPa). The relationship between the permeation flux and time is shown in Fig. 2. It can be seen that the tobacco extract flux decreases gradually in the first 25 min and then approaches to a constant value. Min and Wang (2011) has studied the tobacco extract causes mass transport resistance after the extract is put into the ceramic membrane. The resistance reaches a fixed value when the tobacco extract is evenly distributed in the membrane.

3.2 Electrodialysis process

3.2.1 Na_2SO_4 system

Na_2SO_4 is often used as the electrolyte material in the electrodialysis process for its excellent conductive property. Fig. 3 shows the influence of three kinds of electrolytes on the voltage and current drop across the electrodialysis stack. It can be seen that the stack voltage drop increases gradually with time, indicating salt concentration in the feed chamber is decreased over time. But due to the limitation of the power supply (the maximum voltage supply is 60 V); the constant current mode was not maintained during the entire electrodialysis experiments. The operation mode of the electrodialysis stack was switched from constant current mode to constant voltage mode. It can be seen from Fig. 3 that the currents maintain stable, then decrease with the elapse of time. This indicates that electrolyte in the feed chamber is depleted with the operation of the experiment. Fig. 4 shows the variation of the conductivity with time for three types of electrolytes. The conductivity in the feed chamber is proportion to ions concentration. It explicitly indicates that the dissociated ions in tobacco extract are removed by the electrodialysis process. Table 2

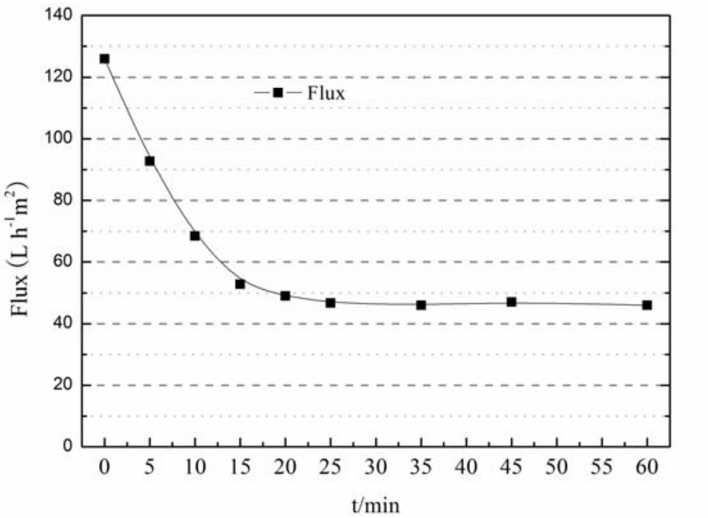

Fig. 2 The relation between the tobacco permeation flux and time

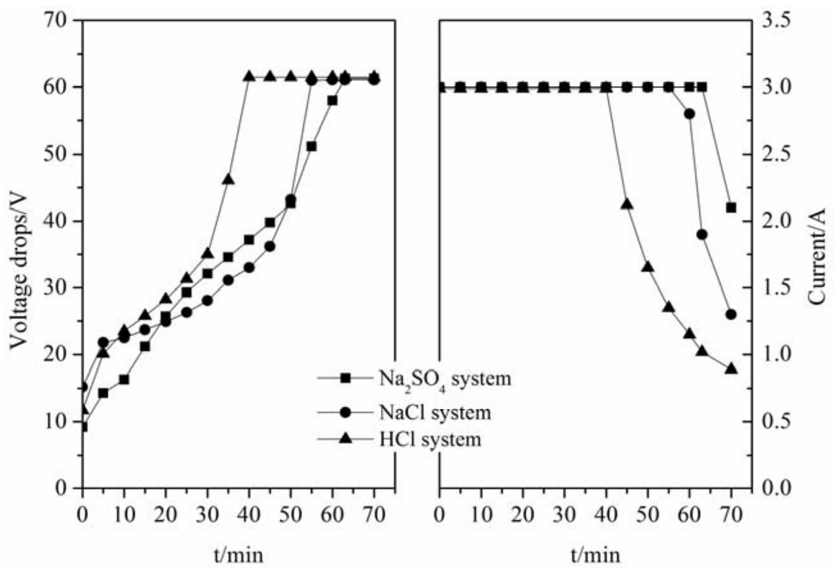

Fig. 3 Effect of three kinds of electrolytes (Na_2SO_4/NaCl/HCl) on the voltage and current drop across the ED stack

shows the desalination rates of chloride and nitrate ions in the feed chamber by using electrodialysis. The removal rates of chloride and nitrate ions are 96.2% and 91.5%, respectively.

But during the experiments, it is found that the solution in concentrated chamber will gradually turn to slight yellow or turbid. An aggregation of suspended particles takes places, and finally a fine, white, flocculent precipitate appears in the late stage of electrodialysis experiment. The possible reason is that the sulfate radical reacts with the metal ions (such as calcium, magnesium

Table 2 The removal rate of the Cl^- and NO_3^-

Type of electrolyte	Removal rate of Cl^-	Removal rate of NO_3^-
Na_2SO_4	96.2%	91.5%
NaCl	81.8%	83.5%
HCl	97.0%	98.4%

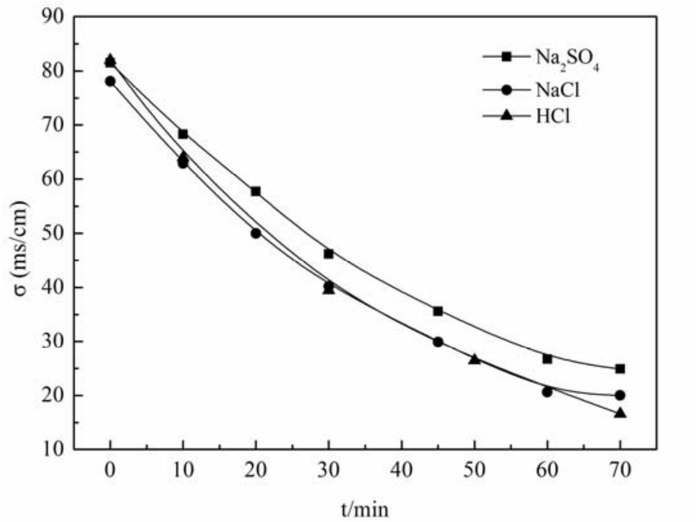

Fig. 4 Effect of three kinds of electrolytes (Na_2SO_4/NaCl/HCl) on desalination rate

and other divalent metal ions) contained in the tobacco extract. This will lead to precipitation at the surface of the membranes. The fouling of the membranes not only induces the permeation flux decreasing but also drastically shortens the membrane life. Therefore, Na_2SO_4 electrolyte is not an appropriate electrolyte for tobacco extract desalination.

3.2.2 NaCl system

In order to prevent precipitation, NaCl solution was chosen as the electrolyte. It can be seen in Fig. 3 that the starting voltage drop is relatively low compared to Na_2SO_4 system. It attributes to slighter equivalent conductivity of chloride ions compared to sulfate ions. It takes less time to reach the maximum value of the direct power supplier. The desalination of tobacco extract with NaCl as electrolyte in Fig. 4 is similar to the case of Na_2SO_4 system. Table 2 shows the removal rates of chloride and nitrate ions with NaCl as electrolyte are 81.8% and 83.5%, respectively. These values are slightly lower than that of the Na_2SO_4 system. Because the NaCl system results in the introduction of chloride ions in the concentrated chamber, the reverse diffusion of chloride ions caused by concentration gradient different leads to the migration of these ions from concentrate chamber to feed chamber. Since the main components of cation and anion ions in the tobacco extract are sodium ions and chloride ions, respectively. The high concentration of sodium and chloride ions in the concentrate chamber will accelerate the back diffusion of these ions from

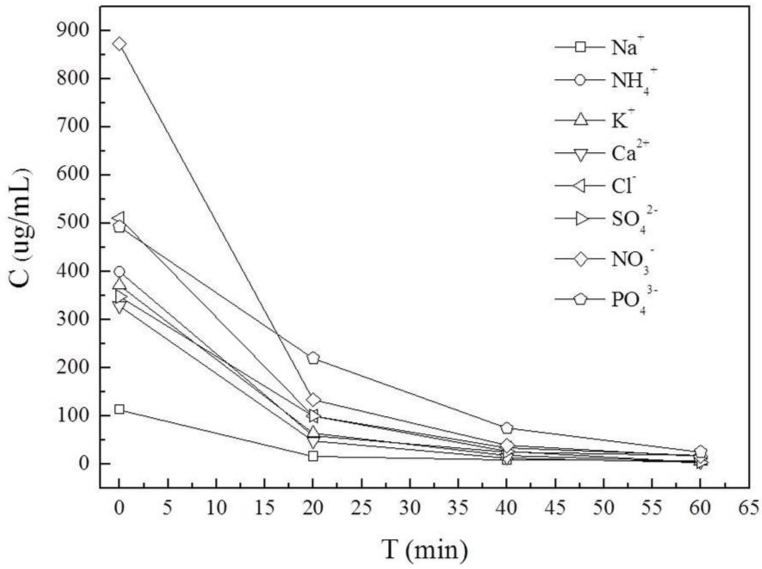

Fig. 5 The time-dependences of the main ions in the tobacco extract with the ED process

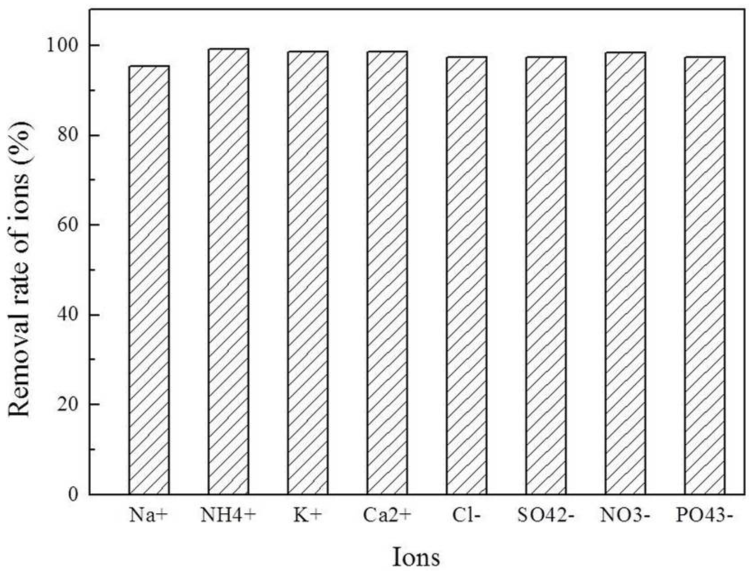

Fig. 6 The removal rate of ions in tobacco extract after electrodialysis

the concentrate chamber into the dilute chamber. This is also the reason for poor performance of desalination when using NaCl as the electrolyte. Consequently, a relatively poor performance of desalination appears. Meanwhile, a white and flocculent precipitate also merges at last. The solution in concentrate chamber is alkaline at the end of the electrodialysis process. This flocculent precipitation disappears after adding strong acid. This phenomenon was called acid-solution and alkali-isolation. The publications (Jiang and Dong 2008, Yildiz 2004, Skott *et al*. 2006) are speculated that this precipitation is nicotine. So, it is necessary to select a more suitable electrolyte to increase the removal rate of undesired anions.

3.2.3 HCl system

Based on the above experiments, hydrochloric acid was chosen as the target electrolyte. The voltage drop increases gradually in the first 40 minutes, then reaches to a plateau. It takes the least time to reach the maximum voltage in HCl electrolyte among the three kinds electrolytes, since the equivalent conductivity of hydrogen chloride ions is greater than that of sodium chloride and sodium sulfate. The desalination curve in this electrolyte is similar to the other electrolytes. The dissociated ions are almost removed by using of electrodialysis. In Table 2, the removal of chloride ions and nitrate ions with HCl as electrolyte reach to 97.0% and 98.4%, respectively. In addition, there no precipitation emerges in the concentrate chamber. Therefore, HCl is a suitable

Table 3 Estimation of the process cost

Parameters	The optimum electrolyte
	HCl
Current density, mA/cm^2	30
Effective membrane area, cm^2	100
Electrolyte (Na_2SO_4) concentration, mol/L	0.3
Fluid flow speed, L/h	300
Experiment time, min	70
Tobacco extracts volume, L	0.4
Repeating units	4
The energy consumption, kW· h/L	0.27
The process capacity, L/year	2633
Electricity charge, $/(kW· h)	0.2
Energy cost, $/L	0.054
Membrane lifetime and amortization of the peripheral equipment, year	3
Anion membrane price,$/$m^2$	200
Cation membrane price, $/$m^2$	170
Membrane cost, $	82.5
Stack cost, $	123.75
Peripheral equipment cost, $	185.63
Total investment cost, $	309.38
Amortization, $/year	103.16
Interest, $/year	24.75
Maintenance,$/year	30.94
Total fixed cost, $/year	158.85
Total fixed cost, $/L	0.06
Total process cost, $/L	0.11

electrolyte for treatment of tobacco extract by using of electrodialysis. Since the ingredients of tobacco and cigarette smoke are very complex as these are over 4000 chemicals in tobacco. It is difficult and time-consuming process to analysis and determination these ingredients (like benzoic acid, sorbic acid, protein and N-nitrosamines). The time-dependences of the concentrations of the main cations and anions in the tobacco extract along with ED process were shown in Fig. 5. The final desalination rates of these ions were indicated in Fig. 6. It is clearly indicated that the undesired ions were almost removed by using the ED technology. The electrodialysis treated tobacco extract is sent to China Tobacco Anhui Industrial Co., LTD for human sensory evaluation. Sensory evaluation results showed that the cigarette made from the electrodialysis treated tobacco sheet has brightly colored, satisfy tobacco fragrance, and better smoking satisfaction.

3.3 Process Economics

Estimation of the operating cost of electrodialysis for tobacco extract desalination is important to determine the economical feasibility of this process. Process cost is calculated according to the literature (Wang *et al*. 2011), and the result is tabulated in Table 3. Energy consumption of process 1 L tobacco extracts is about 0.27 kW·h. The total process cost is only 0.11 $/L, which indicates electrodialysis is a cost-effective technology for treating tobacco extract.

4. Conclusions

A novel electrodialysis process was established for treatment of papermaking tobacco sheet extract. Ceramic filtration was used as pretreatment of tobacco extract. Results indicate that the suspended solids were almost completely removed. The influence of electrolyte solution on the performance of the precipitation was investigated. Finally, 0.1 mol/L HCl at current density of 30 mA/cm^2 was proved to be the optimum condition for tobacco extract desalination. The removal rates of the Cl^- and NO_3^- in tobacco sheet extract were 97% and 98.4%, respectively. The electrodialysis process cost was estimated to be 0.11 $/L. Electrodialysis is a promising, economical and environmentally friendly method to treat the tobacco extracts. However, much more effort is needed to monitor the fouling of the membranes. Nevertheless, electrodialysis technology opens a new dimension to improve the smoking quality of papermaking tobacco sheet extract.

Acknowledgments

The research described in this paper was financially supported in part by the National Natural Science Foundation of China (Nos. 21206154, 21206155), the 6th China Postdoctoral Science Special Foundation (2013T60624), the Fundamental Research Funds for the Central Universities (2013M501058), and the National High Technology Research and Development Program 863 (No. 2012AA03A608).

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