Applied Physics Research
http://ccsenet.org/apr
Vol. 1, No. 2
November 2009

Study on the Experiment of Concentrating Coking Wastewaters by Air-blowing Vacuum Membrane Distillation

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Abstract

In the article, a new air-blowing vacuum membrane distillation (AVMD) process is proposed, and it forms the air-liquid flows in the membrane by forcedly blowing airs to the hot feed liquids circularly flowing in the hollow fiber membrane, and forms the AVMD system to enhance the turbulent degree of the liquids. The intense disturbance of air bubbles and the strong cutting power at the surface of membrane can reduce the depth of the boundary layer of liquids, the temperature and the concentration polarization of the membrane surface, and enhance the speed of heat and mass transfer to enhance the membrane distillation flux and control the membrane pollution. By the process that the optimized AVMD process is used in the coking wastewater treatment process of certain enterprise, the influence of the pretreatment technique of the wastewater on the removal effect of COD is studied in the article, and the influences of the vacuum membrane distillation (VMD) and the AVMD process on the wastewater concentrating treatment effect and efficiency are also respectively researched in the article.

Keywords: Air-blowing vacuum membrane distillation (AVMD), PVDF, Hollow membrane, Hydrophobic membrane, Wastewater treatment

1. Introduction

The membrane distillation (MD) is the membrane separation process combining the membrane technology with the distillation process, and it possesses high interception ratio, and it can realize the distillation process when the negative pressure and the temperature of the feed liquids are very low, and treat reverse osmosis wastewaters with high concentration (Wu, 2003, p.67-75). Most existing researches only aim at the study about the mass transfer process of the steam permeation side, which emphasized to reduce the mass transfer resistance of the membrane/liquid interface of the steam permeation side or enhance the driver of the mass transfer, and few of them study the mass transfer process of the hot side and its strengthening method. J. Phattaranawid and Ma Runyu et al strengthened the turbulent degree of the liquids of the hot side and increased the membrane flux by the pulse feeding method and the feed-liquid-mixing method (M.N. Chernyshov, 2005, P.363-374 & J. Phattaranawik, 2001, P.193-201).

Based on large numbers of theoretical and experimental researches, the AVMD process is designed, and it blows low-pressure compressed airs to the pipes in front of subassembly of the raw water inlet hydrophobic membrane, mixes and forms the two-phase liquids including airs and liquids to enter the subassembly of the hydrophobic membrane, and connects the negative pressure system outside the exit of the producing airs of the hydrophobic membrane subassembly. Taking the demineralization and recycle of the coking wastewaters as the target, and taking the AVMD process as the core, the wastewater treatment process integrating the AVMD process, the chemical flocculation and the super-filtering technology is developed in the article.

2. Experiment

2.1 Main experiment materials and instruments

The main experiment materials and instruments include the PVDF hollow fiber hydrophobic membrane (the interior radius is 0.8m, the exterior radius is 1.1mm, the aperture is 0.160μm, and the porosity is 85%) which is made by the research institute, the hollow fiber membrane subassembly (the effective length is 21cm, the loading rate is 1.51% and the effective membrane area is about 0.025 m^2), the analytical reagent of sodium chloride which is made by the Tianjin Chemical Reagent Factory, the tap water (the conductance value if 230μs/cm, and the water hardness if 15mg/L), the electronic balance which is made by Tianjin Tianma Instruments Factory, and the DDS-11A conductivity meter which is made by Shanghai Rex Instrument Factory.

2.2 Experiment method and data processing

The AVMD process is seen in Figure 1, and the system can be divided into two parts, i.e. the hot side and the cold side, and the hot side is composed by the constant temperature water bathing, the magnetic pump, the liquid flowmeter, the pressure meter, and the subassembly of membrane distillation, which blows airs to the hot feed liquid inlet of the membrane subassembly, and the stable airs controlled by the air valuator enter into the hollow fiber membrane along the flow direction of the hot feed liquid through the air flowmeter. The cold side is composed by the glass condenser, the catchment flume and the vacuum pump.

Heat the feed waters (tap water) to the scheduled temperature in the constant temperature batching, turn on the cycle pumps and the vacuum pumps of the hot side and the cold side, and adjust the flux (flow velocity) of the liquids and the quantity of the airs to the scheduled values. When the temperatures of the inlet and the outlet of two sides of the membrane subassembly are stable, begin clocking and collect the produced waters. Stop the experiment when the quantity of the produced water achieves about 250ml, note the time and measure the conductance rate of the produced water, and respectively compute the membrane distillation flux J and the desalination rate R_j according to the formula (1) and formula (2).

$$J = \frac{W}{S * t} \tag{1}$$

$$R_j = \frac{C_f - C_p}{C_f} * 100\% \tag{2}$$

Where, J (kg/m^2·h) is the membrane flux, W (kg) is the quality of the distillated liquids, S (m^2) is the effective area of membrane, t is the collection time, and C_f , C_p (g/L) respectively are the salt concentrations of the raw feed liquids and the produced waters.

For the air-liquid two phases liquids,

$$\mathrm{Re} = \frac{U_m D}{V_1} = \frac{(qV_Q + qV_L)D}{AV_1} \tag{3}$$

Where, U_m (m/s) is the average flow velocity of the air-liquid two-phase liquids, qV_Q (L/h) is the volume flux of the air phase, qV_L (L/h) is the volume flux of the liquid phase, A (m^2) is the flux area of the pipe section, V_1 (Pa·s) is the movement viscidity of the liquid phase, and D (m) is the equivalent diameter.

3. Results and discussions

3.1 Influence of the air-blowing quantity on the performance of VMD

Under the conditions that the feed liquid temperature is 70℃, the vacuum degree is 0.085MPa, and the flux of the membrane distillation liquids is 120L/h, the influence of air-blowing intension on the performance of membrane distillation process is studied, and the result is seen in Figure 2.

From Figure 2, with the increase of air-blowing quantity, the flux of AVMD process increases significantly. The air-blowing quantity increases from 0 to 70L/h, and the flux enhances double times, from 22kg/m^{2}h to 45kg/m^{2}h. When the liquid flux is fixed, to blow airs to the liquids and form the air-liquid two-phase flow can effectively enhance the turbulent degree of the liquids. According to change of the Reynolds number obtained by the computation method (formula 3) in the air-liquid two-phase flow proposed by Nicklin with the air-blowing quantity (the right coordinate in Figure 2), with the increase of air-blowing quantity, the Reynolds number of the mixed liquids ascend linearly, and when the air-blowing quantity enhances from 0 to 70L/h, the value of Re increases from 2655 to 4204, and the laminar flow develops gradually to the turbulent flow. By the interfering function of air-blowing, the turbulent degree of liquids in the membrane increases, and the cutting forces of the membrane surface are enhanced, and the depth of the boundary layer of the liquids is reduced, and the concentration and the temperature polarization are reduced, so the process flux is enhanced.

At the same time, in the heat transfer process, the boiling heat transfer coefficient is obviously higher than the single phase heat transfer coefficient. According to the reports in the articles (Mandhane J M, 1974, P.537-553 & Kenning D B R, 1972, P.1709-1717), the air-blowing in the convection heat transfer liquids, the heat transfer coefficient can be enhanced for 400%, and the main reason is that the intense interference induced by large numbers of air bubbles can improve the heat exchange of the cold and heat liquids. Because of the analogy character of the heat transfer and the mass transfer, the interfering function of the air bubbles can increase the turbulent degree of liquids, strengthen the cutting force of membrane surface, control the concentration polarization, reduce the membrane pollution and increase the membrane flux.

3.2 Research of the directly concentrating process of coking wastewaters

Under the conditions that the vacuum degree is 0.085MPa, the temperature of the raw water is 70℃ and the flow velocity is 1.0m/s, when the air-water ratios respective are 0 and 0.5, the change performances of the AVMD process with the concentrating time of coking wastewater, the changes of the produced water conductance and PH value in the concentrating process are seen in Figure 3.

From Figure 3, after 900min AVMD concentrating experiment, concentrate the coking waters to initial 5 times concentration, and keep the produced water conductance under 50uS/cm, and the membrane flux descends significantly from 23.7kg/m^{2}h to 16.0kg/m^{2}h. With the increase of concentrating times, the conductance of the concentrating liquids is kept in 35uS/cm to 45uS/cm. But the extent of the PH value of concentrating water changes little relatively, only from 10 to 9.38.

3.3 COD removal and its concentrating process of coking wastewaters

To reduce the organic matters' accumulation in the concentrated coking wastewater to pollute the membrane and reduce the flux and produce CODcr, in this experiment, different flocculating agents are appended to the coking wastewaters to removal CODcr, and the results are seen in Figure 4 and Figure 5.

From Figure 4, with the increase of PFS quantity, the CODcr value of the raw water descends, and when the quantity achieves 100mg/l, the value of COD is 700mg/l, and the removal rate of corresponding COD is 64.7%. From Figure 5, with the increase of PAC quantity, the COD value of raw waters first decreases and then ascends, and when the quantity of PAC is 75mg/l, the value of COD is 500mg/l, and the corresponding COD removal rate is 74.7%. So, under normal temperature, when the appended quantities are same, the removal effect of PAC for raw water COD is better than PFS.

The optimal appended quantity of PAC is 75mg/l, and under the conditions that the vacuum is 0.085MPa, the temperature of raw water is 70℃, the flow velocity is 1.0m/s, and the air-blowing intension if 50L/h, the results of the AVMD concentrating experiment for removing CODcr in coking wastewaters are seen in Figure 6 and Figure 7.

From Figure 6 and Figure 7, in the initial of the AVMD concentrating process, the membrane flux descends slowly, and after 700min's concentrating, the wastewaters removing CODcr are concentrated five times, the produced water conductance in the concentrating process is kept under 10μS/cm, and the membrane flux descends from initial 29.1kg/m^{2}h to 18.2kg/m^{2}h. With the increase of concentrating times, in the process that the raw waters are concentrated five times, the conductance of concentrated water decrease from initial 50uS/cm to 28uS/cm. In the concentrating process, the COD of concentrating water ascends from 500mg/L to 2300mg/L, and the CODcr of produced waters is stabilized in 1.7mg/L-2.1mg/L because the raw waters contain certain volatile low-molecule organic matters which can enter into the produced waters through the membrane holes.

In conclusion, the decrease of the VMD flux may come from the influence of the descending steam pressure, and the mass transfer driver of the membrane distillation process is the water steam pressure difference between two sides of the membrane, and when the distillation object is watery liquids, the influence of the descending steam pressure can be ignored, but when the concentration of the liquids is high, the descending steam pressure of the liquids will reduce the water steam pressure difference between two sides of the membrane, which will reduce the VMD flux. On the other hand, in the VMD concentrating process, the concentration of the inorganic-salt and the organic matters in the concentrating waters increase, and because of the increase of the concentration difference polarization effect, the membrane flux will decrease even the membrane pollution will be induced. But in the AVMD process, the air-liquid two-phase flow formed by air-blowing will change the laminar flows of the membrane cavity to the turbulent flows, and the high-effective convection mass transfer will replace single molecule diffusion, and the heat transfer process is changed from heat exchange to heat flow transfer, and the boundary layer and the temperature boundary layer effect will be minified, so the membrane flux will be reduced and the membrane pollution will be reduced.

4. Conclusions

The PVDF hollow fiber hydrophobic micro-hole membrane is adopted to design the AVMD process in the article, and the concrete process is that: blow low-pressure compressed airs to the pipes in front of subassembly of the raw water inlet hydrophobic membrane, mix and form the two-phase liquids including airs and liquids to enter the subassembly of the hydrophobic membrane, and connect the negative pressure system outside the exit of the producing airs of the hydrophobic membrane subassembly. Comparing with general VMD process, the blowing function of the compressed air can change the mass transfer principle of the water steam of two sides of the hydrophobic membrane in the membrane subassembly, which can enhance the membrane penetration transfer speed of the water steam and the flux of the membrane distillation.

The research result shows that the self-made high-flux PVDF hollow fiber hydrophobic micro-hole membrane can be used to treat the coking wastewaters in the AVMD process. The organic matter content in the wastewaters is higher, which is the main reason to reduce the flux in the AVMD process, and the proper treatment can remove CODcr and keep the membrane flux. Under the conditions that the vacuum degree is 0.085MPa, the temperature of the raw water is 70℃ and the flow velocity is 1.0m/s, the AVMD process flux of the pretreated coking wastewaters can achieve 30.8kg/m^{2}h, and when the concentration achieves 5 times, the flux is kept in 18.6kg/m^{2}h, and the conductance of produced waters is kept under 10μS/cm, and the CODcr of produced water is stabilized in 2mg/L-4 mg/L.

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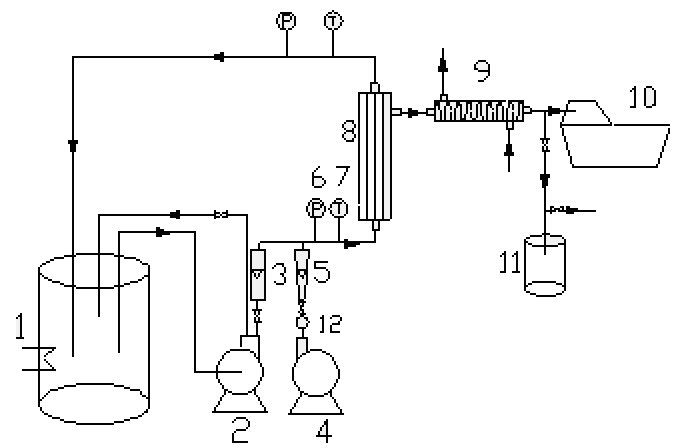

Figure 1. Experimental Apparatus for AVMD Process

(1: Flume of materials, 2: Magnetic pump, 3: Liquid flowmeter, 4: Air pump, 5: Air flowmeter, 6: Pressure meter, 7: Thermometer, 8: Subassembly of hollow fabre membrane, 9: Condensation pipe, 10: Vacuum pump, 11: Catchment flume, 12: Valuator)

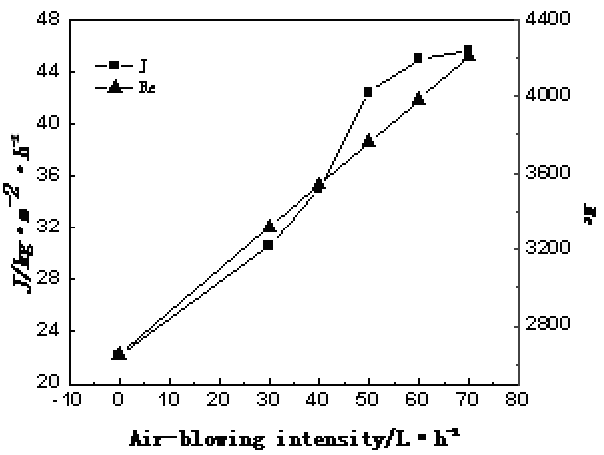

Figure 2. Influence of Air-blowing Quantity on the Membrane Distillation Performance

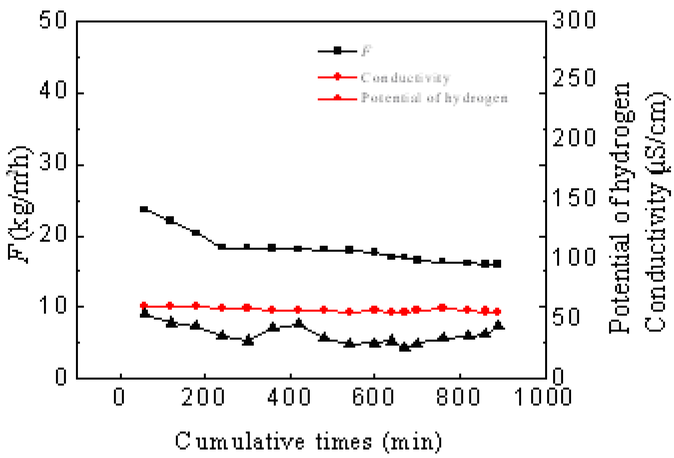

Figure 3. Influence of Operation Time on the AVMD Process

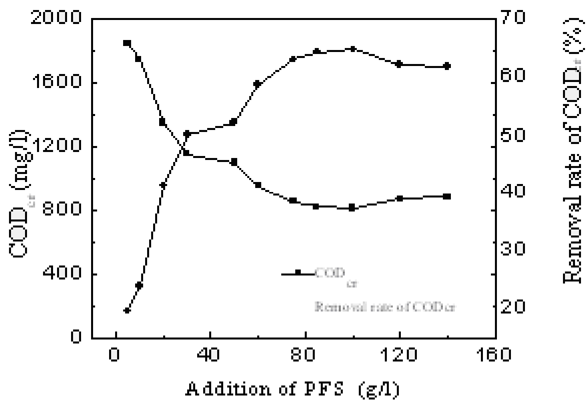

Figure 4. Influence of PFS Quantity on the value of CODcr and the removal rate of CODcr

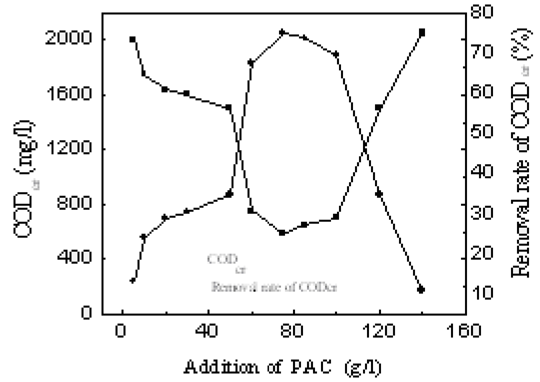

Figure 5. Influence of PAC Quantity on the value of CODcr and the removal rate of CODcr

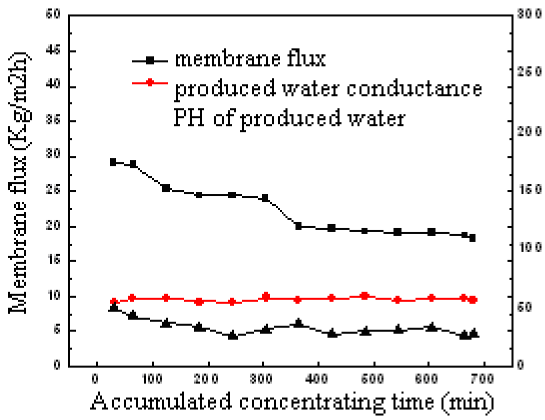

Figure 6. Condensing Five Times after Appending the Flocculating Agent PAC

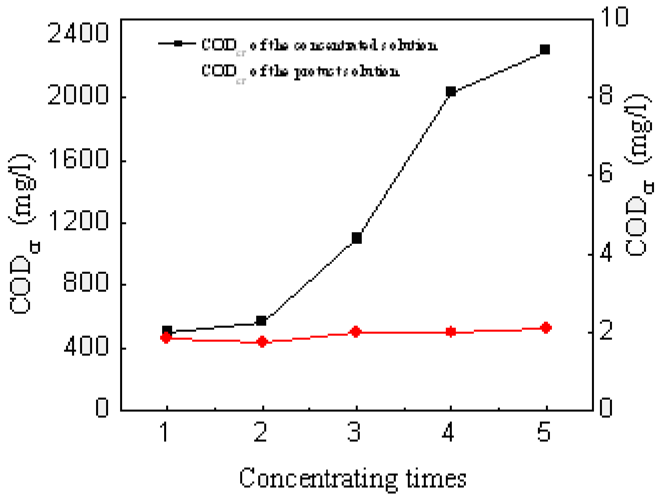

Figure 7. Changes of CODcr of the Produced Water and the Concentrated Water