Treatment of heavy-metal wastewater by vacuum membrane distillation: effect of wastewater properties

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Abstract. Heavy metal wastewater is a common byproduct in heavy metal industries. Membrane distillation is considered as promising technology to treat such wastewater. The treatment of heavy metal wastewater by vacuum membrane distillation (VMD) was conducted in this work. The effects of pH, calcium and EDTA on VMD performance were investigated. VMD process showed a good acid resistance as the solution pH above 0. When the solution pH was 0, the permeate conductivity was below 40μS·cm⁻¹. Calcium and EDTA were found to have influence on VMD performance to some extent. VMD process was proved to be suitable for heavy metal wastewater as long as the impurity content was in control of a certain degree.

1. Introduction

Heavy metal wastewater is a common byproduct in heavy metal industries. Chemical precipitation is commonly used to treat such wastewater. However, solid waste produced in the process of chemical precipitation easily causes secondary pollution to the environment [1]. Besides, the loss of heavy metal resources is also worth paying attention. Recovering water and heavy metal should be the target to treat such wastewater. Thus, one kind of technology which can realize concentration and distillation is necessary. Membrane distillation is such a technology exactly, which uses hydrophobic membrane materials as separation membrane [2,3].

In contrast to reverse osmosis (RO), membrane distillation has better separation efficiency and higher concentration ratio. Membrane distillation includes several operation modes. Vacuum membrane distillation (VMD) is a very common operation mode in laboratory research [4].

At present, there is few work on the treatment of heavy metal wastewater by VMD. The heavy metal wastewater has a lower pH and contains many heavy metal ions, such as Zn²⁺, Ni²⁺, Cr (VI), and Fe (III) etc., as well as organic acids [5,6]. In consideration of the complexity of heavy metal wastewater, investigating the effect of wastewater properties on vacuum membrane distillation is significant.

2. Experimental

2.1. Materials

A kind of PTFE hollow membrane, which was provided by Zhejiang Dongda Environment Engineering Co., Ltd, China, was chosen to fabricate hollow fiber membrane modules. The
characteristics of the membrane are presented in Table 1. The effective membrane areas of all modules in this work are 0.018 m².

2.2. Methods
The VMD experimental equipment was self-made. A series of manual solutions as displayed in Table 2 containing all or part of Zn²⁺, Ni²⁺, Cu²⁺, Ca²⁺ and EDTA was prepared as the feed solution of VMD. Then, a batch of experiments were conducted on the VMD system to investigate the influences of wastewater properties on the VMD performance. Process parameters were set as below: feed temperature 57°C, feed velocity 0.7 m·s⁻¹, vacuum degree -93 KPa.

| Membrane material | PTFE |
|------------------|------|
| Nominal pore size (μm) | 0.243 |
| Thickness (μm) | 440 |
| Porosity (%) | 40 |
| Outer diameter (mm) | 1.72 |
| Inter diameter (mm) | 0.84 |
| Contact angle (°) | 101 |

Table 1. The characteristics of the membrane material

| Solution no. | Zn (mg·L⁻¹) | Ni (mg·L⁻¹) | Cu (mg·L⁻¹) | Ca (mg·L⁻¹) | EDTA (mg·L⁻¹) |
|--------------|-------------|-------------|-------------|-------------|---------------|
| S-I          | 600         | 200         | 400         | /           | /             |
| S-II         | 3000        | 1000        | 2000        | /           | /             |
| S-III        | 600         | 200         | 400         | 100         | /             |
| S-IV         | 3000        | 1000        | 2000        | 500         | /             |
| S-V          | 600         | 200         | 400         | 100         | 300           |

Table 2. Chemical constituents and contents of manual solutions (mg·L⁻¹)

3. Results and discussion

3.1. Effect of solution pH
Heavy metal wastewater usually has a high degree of acidity. The effect of pH on the VMD performance is worth paying attention. Based on S-I, solutions with four levels of pH: 4.8, 2, 1, 0 were prepared as VMD feed. The permeate flux and conductivity at each hour in the VMD process were monitored. The results are shown in Fig. 1.

![Fig. 1 Effect of pH on permeate flux and conductivity in VMD process. (a, permeate flux; b, permeate conductivity)](attachment://image.png)
The permeate flux is slightly decreasing with the varying of pH from 4.8 to 0 (Fig. 1a). The permeate conductivity is slightly increasing with the varying of pH from 4.8 to 0 (Fig. 1b). What is more, the permeate flux and conductivity are stable and keep at a good level in the whole process, which indicates that high acidity has no significant influence on VMD performance. Based on PTFE hollow fiber membrane, VMD process has a good acid resistance.

3.2. Effect of calcium
Calcium is a common element in wastewater. For sulfuric acid system, the effect of calcium sulfate micro solubility on VMD performance should be concerned. So, the effect of calcium in the solution on VMD performance was investigated in this section. VMD process was conducted with solution S-III and S-IV as feed. The permeate flux and conductivity at each hour in the VMD process were monitored. The results are shown in Fig. 2.

![Fig. 2 Effect of calcium on permeate flux and conductivity in VMD process. (a, Ca^{2+} 100 mg·L^{-1}; b, Ca^{2+} 500 mg·L^{-1})](image)

Fig. 2 shows that the permeate conductivity for both solution stay within 10 μS·cm^{-1} in the whole process. However, for the solution with Ca^{2+} of 100 mg·L^{-1}, the permeate flux stays nearly 5.6 kg·m^{-2}·h^{-1}, while the permeate flux drops 20% in the end of the whole process for the solution with Ca^{2+} of 500 mg·L^{-1}. It was observed that sediment produced in the process for the solution with Ca^{2+} of 500 mg·L^{-1}. The results indicate that high concentration of Ca^{2+} in wastewater is not advantage for VMD process.

3.3. Effect of EDTA
EDTA is often used in electroplating industry to control the concentration of metal ions. In heavy metal wastewater, metal ions and EDTA easily format complex compound. EDTA is both an organic matter and carboxylic acid. In this section, the effect of EDTA on VMD performance is investigated. VMD process was conducted with solution S-III and S-V as feed. The permeate flux and conductivity at each hour were monitored. The results are shown in Fig. 3.
Fig. 3 Effect of EDTA on permeate flux and conductivity in VMD process. (a, no EDTA; b, EDTA 300 mg·L\(^{-1}\))

Fig. 3 shows that EDTA has almost no influence on permeate flux, but has obvious effect on permeate conductivity. For the solution with EDTA of 300 mg·L\(^{-1}\), the permeate conductivity is up to 90.6 \(\mu\)S·cm\(^{-1}\) from 6.4 \(\mu\)S·cm\(^{-1}\) in the whole process. The results indicate that EDTA will cause VMD performance worsen. The controlling of EDTA content in the wastewater is necessary for VMD process.

4. Conclusion
VMD process was applied to deal with heavy metal wastewater. The effect of wastewater properties containing pH, calcium and EDTA on VMD performance was investigated in this work. Based on PTFE hollow fiber membrane, VMD process showed a good acid resistance as the solution pH above 0. However, calcium and EDTA had influence on VMD performance to some extent. The research indicates that the controlling of calcium and EDTA content in the wastewater is necessary for VMD process.

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References
[1] Wang T, Li X G, Du Q Y. Research progress in treatment technologies for heavy metal ion containing wastewater. Environmental protection of chemical industry. 2008,28 (4):323-326.
[2] Lawson KW, Lloyd DR. Membrane distillation [J]. Journal of Membrane Science. 1997,124 (1):1-25.
[3] Alkhudhiri A, Darwish N, Hilal N. Membrane distillation: A comprehensive review. Desalination. 2012,287 (0):2-18.
[4] Liu J, Wu C R, Lv X L. Heat and mass transfer in vacuum membrane distillation. CIESC Journal. 2011,62 (4):908-915.
[5] Fu F, Wang Q. Removal of heavy metal ions from wastewaters: A review [J]. Journal of Environmental Management. 2011,92 (3):407-418.
[6] Barakat MA. New trends in removing heavy metals from industrial wastewater [J]. Arabian Journal of Chemistry. 2011,4 (4):361-377.