Removal of Cu (II) From Aqueous Solution by Rotating Disk Shear Enhanced Complexation-Ultrafiltration

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Abstract. The polyacrylic acid sodium (PAAS) has been applied into the removal of Cu (II) from aqueous solutions by a rotating disk shear enhanced complexation-ultrafiltration process. As important factors, solution pH and polymer/metal mass ratio (P/M) on the rejection of Cu(II) have been investigated, the removal rate of Cu (II) can reach 99.6% at suitable condition, pH=6.0, P/M=25. The permeate flux increases from 38.5 to 47.2 L·m⁻²·kPa⁻¹·h⁻¹ with the increase of rotating speed from 0 to 3000 rpm. However, the rejections of Cu (II) decrease sharply when the rotating speeds are more than 700, 900, 1000 rpm at pH values 4.0, 5.0, 6.0, respectively. Thus, only at suitable rotating speed, can high permeate flux and removal rate be obtained for shear enhanced complexation-ultrafiltration.

1. Introduction

Metal plating wastewater streams contain a large amount of Cu (II) [1]. Cu (II) causes serious problems to human [2]. Chemical precipitation, adsorption, ion-exchange are some of the most commonly used processes and have obvious disadvantages [3]. Complexation-ultrafiltration, one of the membrane technologies, makes possible to separate, concentrate and recover selectively some heavy metal ions from a variety of aqueous streams [4].

Dynamic filtration consists in creating the shear rate at the membrane by a relative motion between the membrane and a moving part [5]. M.Y. Jaffrin et al. [6] have showed that rotating disk yields better performance than the vibratory shear enhanced processing. Zhen-zhou Zhu et al. [7] used a rotating disk module in MF and UF of chicory juice. Compared with dead end filtration, the rotating disk module had a much higher permeate flux.

Although removal of heavy metals by complexation-ultrafiltration has been widely investigated, this work was the first one using a rotating disk module in complexation-ultrafiltration of Cu (II). The effect of operating conditions such as rotating speed, polymer/metal mass ratio (P/M) and pH on the filtration efficiency for Cu (II) was investigated in this paper.

2. Experimental

2.1. Chemicals, experimental set-up and membrane

Polyacrylic acid sodium (Polymerization Degree 2700~7500) was selected to be polymeric agent. Cu (NO₃)₂·3H₂O was used as sources of Cu (II), and the initial concentration of Cu (II) is 10 mg/L for all
the solutions if no explanation is given. Polymer solution was pre-treated using the PES hollow ultrafiltration membrane (MWCO 30kDa).

The filtration test set-up is represented in Figure 1(a). The parameters of the flat membrane are given in Table 1. The rotating disk membrane separation system in laboratory is shown in Figure 1(b). The filtration module consists of an 88 mm inner radius circular housing inside with a disk rotates. The disk radius and thickness are 83 mm and 4 mm, respectively.

| Membrane type         | Molecular weight cut-off (kDa) | Outside diameter (mm) | Insider diameter (mm) | Surface area (m²) |
|-----------------------|-------------------------------|-----------------------|-----------------------|------------------|
| polyethersulfone(PES) | 30                            | 180                   | 14                    | 0.0253           |

Figure 1. (a) Schematic of filtration system

Figure 1. (b) Schematic of rotating disk module
2.2. Calculation of shear rate on membrane
In the module, the flow field taken on an inviscid core rotating at a velocity of \( k\omega \), where \( \omega \) is the disk angular velocity (rad/s) and \( k \) is velocity factor [8]. The local characteristic Reynolds constant number \( Re \) for the flow near the membrane is defined as:

\[
Re = \frac{k\omega r^2}{\nu}
\]  \( (1) \)

Where \( \nu \) denotes kinematic viscosity (m\(^2\)·s\(^{-1}\)).

According to Itoh et al., the factor \( k \) in the rotating disk is independent of the radius [9], and is determined by peripheral pressure, satisfying Bernoulli equation in the inviscid core:

\[
P_p = 0.5\rho k^2\omega^2 r^2 + P_0
\]  \( (2) \)

Where \( P_0 \) is the center pressure.

The shear rate on the stationary membrane were calculated by Bouzerar et al. [10] in the laminar regime (\( N<570 \) rpm) and turbulent regime (\( N>570 \) rpm). The results were found as

\[
\gamma_{ml} = 0.77\nu^{-0.5}(k\omega)^{1.5}r
\]  \( (3) \)

\[
\gamma_{mt} = 0.0296\nu^{-0.8}(k\omega)^{1.8}r^{1.6}
\]  \( (4) \)

Where \( \gamma_{ml} \) is the shear rate in the laminar regime and \( \gamma_{mt} \) is the shear rate in the laminar regime.

3. Results and discussion

3.1. Determination of factor \( k \) and membrane edge shear rate
The variations of pressures with rotation speed at the radii of 0.029, 0.059 and 0.088m, \( P_o=0.01\)MPa, \( \text{pH}=7.0 \) and \( P/M=25 \) are represented in Figure 2(a). As shown in Figure 2(a), the pressure values elevate with the increasing rotation speed and the peripheral pressure (\( r=0.088m \)) is most changeable.

The relationships between the local radial pressure \( P_i \) and \( \omega \) can be fitted at a certain radius, and the fitting function is obtained:

\[
P_i = 311\omega^2 r^2 + 10000
\]  \( (5) \)

The kinematic viscosity of test fluid is \( 1.46\times10^{-6} \) m\(^2\)·s\(^{-1}\) at \( 25^\circ\)C. In the turbulent regime, the edge \( \gamma_{mt} \) is calculated by Eq. 4. As shown in Figure 2(b), shear rates increases with the increasing rotating speed and the highest peripheral shear rate is \( 577487 \) s\(^{-1}\) at 3000 rpm.
3.2. Effects of solution pH and P/M on the rejection of Cu (II)

Figure 3(a) shows the effect of pH on the rejection at 500rpm and P/M=25. It is clearly observed that the Cu (II) rejections are enhanced with the increase of the pH. As shown in Figure 3(a), the Cu (II) rejection is greater than 99.6% at the P/M=25 and pH=6.0.

The influences of P/M on rejection of Cu (II) and permeate flux at 500rpm and pH=6.0 is depicted in Figure 3(b). One can see that the Cu (II) rejections go up with the increase of the P/M, but the rejection of Cu (II) remains nearly 99.6% with respective P/M of 25 and 30. And for the permeate flux, it is can be seen a little decline of the permeate flux with the increase of the P/M, which is caused by the increase of viscosity of the solution.

3.3. The effect of rotating speed on the permeation and the rejection of Cu (II)

Higher rotating speed is always accompanied with higher shearing force on membrane surface, which can help to reduce or remove the membrane fouling and concentration polarization and improve permeate flux [6], but the high enough shear rates may make PAA-Cu dissociated, which results in a decline of rejection. The permeation (pH=6.0, P/M=25 and 30L/h) and the rejection of PAAS were shown as Figure 4(a). It can be clearly seen from Figure 4(a) that the permeation is 38.5 L·m⁻²·kPa⁻¹·h⁻¹ at rest while that increases to 47.2 L·m⁻²·kPa⁻¹·h⁻¹ at 3000 rpm and the rejections of PAAS remain

![Figure 2](image2.png)

![Figure 3](image3.png)

![Figure 4](image4.png)
~99.5% with the rotating speed changes, only a little PAAS which has a low degree of polymerization can transmit to the membrane. The results indicate that the high rotating speed produced high shear rate on membrane surface, enhancing the permeate flux. And the rejection of PAAS has been not affected by the shear rate at various pH values when the rotating speed is lower than 3000 rpm.

Figure 4. (a) The effect of rotating speed on the rejection of PAAS and the permeation; (b) Variation of the rejection of Cu (II) with rotating speed

Figure 4(b) shows the variation of the rejection of Cu (II) with rotating speed from 0 to 3000 rpm. It is clearly seen that, once the speed exceeds a certain value, \( R_{\text{Cu}} \) decreases sharply. At pH 4.0, 5.0 and 6.0, PAA-Cu can keep stable below the rotating speeds of 700 rpm, 900 rpm and 1000 rpm, respectively. It seems that the rejection of Cu (II) increases with pH. The lower pH values facilitate the decomplexation of the PAA-Cu, and conversely, the complexation reaction of Cu (II) and [-COO\(^-\)] is enhanced. Obviously, the removal efficiency depends on the solution pH values and the rotating speeds.

4. Conclusion
The polyacrylic acid sodium was applied into the removal of Cu (II) from aqueous solutions by a rotating disk shear enhanced complexation-ultrafiltration process. With the increase of the rotating speed, the concentration polarization and membrane fouling decrease, and the permeation flux increases. The permeate flux increases from 38.5 to 47.2 \( \text{L} \cdot \text{m}^{-2} \cdot \text{kPa}^{-1} \cdot \text{h}^{-1} \) with the increase of rotating speed from 0 to 3000 rpm. The rejection of Cu (II) could arrive at 99.6% at the optimal operation condition pH=6.0, P/M=25. However, the rejections of Cu (II) decreased sharply when the rotating speeds were more than 700, 900, 1000 rpm at pH values 4.0, 5.0, 6.0, respectively. This may be the dissociation of PAA-Cu complex when the rotating speed exceeds a certain value. Thus, only at suitable rotating speed, can high permeate flux and removal rate be obtained for shear enhanced complexation-ultrafiltration using rotating disk membrane.

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