Selective Separation of Cu (II) and Cd (II) from Aqueous Solution by Shear Induced Dissociation and Ultrafiltration Using Rotating Disk Membrane

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Abstract: Selective separation of Cu (II) and Cd (II) from aqueous solution by shear induced dissociation and ultrafiltration have been investigated using rotating disk membrane (RDM) and polyacrylic acid sodium (PAAS) as complexing agent. The shear rate distribution on the membrane surface has been calculated at a certain rotating speed. The polymer-metal complex can dissociate when the shear rate exceeds the critical shear rate ($\gamma_c$), the smallest shear rate at which the polymer-metal complex starts to dissociate. The difference of the critical shear rates of the polymer-metal complexes can be used to separate different metal ions from aqueous solution. The critical shear rate of PAA-Cd complex ($\gamma_{Cr}$) is greater than that of PAA-Cu complex ($\gamma_{Cu}$) at pH 6.0. Cu (II) and Cd (II) can be separated when shear rate is greater than 8.0x10$^4$ s$^{-1}$ at pH 6, P/M 27.5. Moreover, the regeneration of PAAS has been also finished at $\gamma$>1.31x10$^5$ s$^{-1}$. Compared with the acidification, shear induced dissociation, is a novel and green technology for recovery of heavy metal ions and polymer from aqueous solutions without the consumption of acid and alkali.

1 INTRODUCTION

Electroplating wastewater streams contain much Cu (II) and Cd (II), which are harmful to human (Manis, et al., 2013). Complexation-ultrafiltration is an excellent way to remove heavy metals due to its high efficiency and no secondary pollution (Qiu and Mao, 2013). It is necessary to separate various heavy metal ions in the treatment of wastewater for the recovery of metal ions.

The inorganic acids are used to acidify the complexes solution and then diafiltration experiments is performed to recover polymer and heavy metal in conventional acidification decomplexation method (Shao, et al., 2013), but it is easy to cause secondary pollution due to the use of the chemicals of acid and alkali, and is not convenient for the recovery of heavy metals.

In our previous work, polyacrylic acid sodium (PAAS) is applied to remove various heavy metal ions from aqueous solutions by complexation-ultrafiltration using rotating disk membrane (RDM). RDM filtration consists in creating the shear rate on the membrane surface by a relative motion between the fixed membrane and a disk rotating (Jaffrin, 2008). The stabilities of polymer-metal complexes in the shear field have been studied and the results show that the polymer-metal complexes can dissociate when the shear rate is higher than the critical shear rate $\gamma_c$, the smallest shear rate at which the polymer-metal complex starts to dissociate (Gao et al., 2018; Chen and Qiu, 2018; Tang and Qiu, 2018). In this work, shear induced dissociation and ultrafiltration, is applied to separate Cu (II) and Cd (II) and regenerate PAAS from the mixed aqueous solution, which is novel and green technology without the consumption of acid and alkali.

2 EXPERIMENTAL

2.1 Chemicals, Membrane and Set-up

PAAS with average molecular weight 250 kDa was purchased from Wako Pure Chemical Industries, Japan. The PAAS solutions were pretreated by diafiltration to remove small molecular weight PAAS. Cadmium nitrate tetrahydrate and copper...
nitrates were used to prepare the aqueous solution. Hydrochloric acid and sodium hydroxide were used to adjust aqueous pH. All solutions in the experiment were prepared with deionized water. Polyether sulphone (PES) flat ultrafiltration membrane with MWCO 10 kDa was supplied by Shanghai Yuling Filter Equipment Co, Ltd.

The device consists of a cylindrical housing containing a metal disk. The rotating shaft which connects with the motor outside the housing is located at the centre of feed inlet side of the housing and can provide the rotating speed of 0-3000 rpm. The flat PES ultrafiltration membrane is fixed on the retentate outlet side of the cavity. The depth of housing is 30 mm, and the inner radius of the housing is 88 mm which is same as the radius of the membrane. The detailed structure is shown in Figure 1. The radius of the rotating disk is 80 mm, the thickness is 4 mm, the six blades are evenly distributed around the centre of the disk and the blade height is 2 mm and the distance from the membrane surface is 14 mm.

Figure 1: Schematic of filtration device.

2.2 Experimental Procedure

The metal ions fully reacted with polymers after two hours under the specified pH and P/M (mass ratio of polymer to metal ions) conditions, and then pumped into the device by peristaltic pump. The concentrations of metal ions were 10 mg/L. According to our previous studies (Chen and Qiu, 2018; Tang and Qiu, 2018), the separation efficiency of Cu (II) and Cd (II) was investigated using 550 mg/L PAAS and pH=6.0 to make heavy metal completely complexed in a static filtration. At pH 6.0, the critical shear rates of PAA-Cd complex (γ_{c,Cd}) and PAA-Cu complex (γ_{c,Cu}) were 8.0x10^4 s^{-1}, 1.31x10^5 s^{-1}, respectively. The initial operating pressure of the device was controlled at 10 kPa. Then, the diafiltration experiments were carried out at different rotating speeds to separate Cu (II) and Cd (II) and regenerate PAAS. The concentration of PAAS was measured with chemical oxygen demand (COD). The concentration of heavy metal was measured by atomic absorption spectrophotometry. All experiments were carried out at 25°C.

3 RESULTS AND DISCUSSION

3.1 The Shear Rate on the Membrane Surface

The distributions of shear rate on the membrane surface was explored by the recent research of the present authors (Tang and Qiu, 2018).

\[ \gamma_{ml} = 0.77 \nu^{0.5} (k \omega)^{1.5} r \]  
\[ \gamma_{ml} = 0.0296 \nu^{0.8} (k \omega)^{1.8} r \]

where \( \gamma_{ml} \) and \( \gamma_{ml} \) represent the shear rates at laminar and turbulent state, respectively (s^{-1}), \( \nu \) is kinematic viscosity of test fluid (m^2/s), \( k \) is the angular velocity of the disk (rad/s), \( r \) is the radius (m). The velocity factor \( k \) of the six rectangular blades is 0.79 (Chen and Qiu, 2018; Tang and Qiu, 2018).

Figure 2 shows the variation of the shear rate on the edge of membrane surface with rotating speed. The shear rate increases with the rotating speed.

3.2 Effect of Rotating Speed on the Rejection of Cu (II) and Cd (II)

In the previous studies, the rejection of Cu (II) was 99.5% when the rotating speed was lower than 1000 rpm at pH 6.0, P/M=25, and the rejection of Cd (II) could reach 99.7% when the rotating speed was less than 1320 rpm at pH 6.0, P/M=30 (Chen and Qiu, 2018; Tang and Qiu, 2018). Effect of rotating speed on the rejection of Cu (II) and Cd (II) was investigated using 550 mg/L PAAS and pH 6.0 to make heavy metal ions completely complexed in a
static filtration. As shown in Figure 3, the $R_{Cu}$ remains stable when the rotating speed is lower than 1000 rpm, while the $R_{Cd}$ has a sudden drop when the rotating speed exceeds 1000 rpm. Similar variations can be found in $R_{Cd}$.

![Figure 3: Effect of rotating speed on the rejection of Cu (II) and Cd (II) (pH 6.0, P/M=27.5).](image)

The critical shear rate of complexes is the smallest shear rate at which the complex begins to dissociate and the value is only related to the geometry of the device at a certain pH. So, the critical shear rates ($\gamma_c$) of PAA-Cu and PAA-Cd at pH 6.0 can be calculated by Eqs. (1) and (2), and the calculation results are shown in Table 1. The critical shear rate of PAA-Cd is greater than that of PAA-Cu, indicating that the shear stability of PAA-Cd is stronger than that of PAA-Cu at pH 6.0. The experimental results provide support for the following shear induced separation.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\gamma_c$ / s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAA-Cu complex</td>
<td>8.0x10$^4$</td>
</tr>
<tr>
<td>PAA-Cd complex</td>
<td>1.31x10$^5$</td>
</tr>
</tbody>
</table>

### 3.3 Selective Separation Coefficient

The selective separation coefficient (Uludag, et al., 1998) ($\beta_{Cu/Cd}$) of the both metals can be defined as:

$$\beta_{Cu/Cd} = \frac{1 - R_{Cd}}{1 - R_{Cu}}$$

where $R_{Cu}$ and $R_{Cd}$ are Cu (II) and Cd (II) rejections, respectively.

$\beta_{Cu/Cd}$ obtained at rotating speed from 0 to 3000 rpm at pH 6.0 is shown in Figure 4. It is clearly seen that $\beta_{Cu/Cd}$ firstly keeps invariable when the rotating speed is lower than 1000 rpm, but after this it shows a remarkable increase followed by a significant drop. This can be explained as follows: when the shear rate on the membrane surface is lower than the critical shear rate of PAA-Cu complex and PAA-Cd complexe, both of the PAA-Cu complex and PAA-Cd complex remain stable. When the rotating speed exceeds 1000 rpm, the shear rate on the membrane surface is higher than the critical shear rate of PAA-Cu complex, causing the dissociation of the PAA-Cu complex and the decrease of $R_{Cu}$, while PAA-Cd complex remains stable and $R_{Cd}$ keeps constant. Therefore, $\beta_{Cu/Cd}$ shows an enlargement trend. When the shear rate is higher than the critical shear rate of PAA-Cd complex, PAA-Cd complex also begins to dissociate, $R_{Cd}$ declines and $\beta_{Cu/Cd}$ also decreases. Therefore, it may be preferable for selective separation to choose a suitable rotating speed, such as 1300 rpm, at which the shear rate is between 8.0x10$^4$ s$^{-1}$ and 1.31x10$^5$ s$^{-1}$. The greatest selection separation coefficient can be obtained at 1300 rpm, as shown in Figure 4.

![Figure 4: Effect of rotating speed on selective separation coefficient $\beta_{Cu/Cd}$.](image)

### 3.4 Selective Separation of Cu (II) and Cd (II) and Regeneration of PAAS by Shear Induced Dissociation and ultrafiltration

The selective separation and the regeneration experiments were carried out at pH 6.0 and P/M=27.5. In rotating disk diafiltration experiments, an amount of de-ionized water was add to the feed tank simultaneously and continuously to keep the volume of the feed remain constant. The rotating speed was adjusted to 1300 rpm for diafiltration experiments to separate Cu (II) and Cd (II).

The PAA-Cu complex easily dissociates due to its smaller critical shear rate, and the free Cu (II) permeates the membrane into the permeate. Figure 5 is the variation of the concentration of residual copper (C$_{Cu}$) and the concentration of cadmium (C$_{Cd}$) in the retentate with the volume of make-up water (V$_{m}$) at 1300 rpm. It can be seen that C$_{Cu}$ decreases obviously but C$_{Cd}$ keeps constant,
because PAA-Cu complex dissociates and PAA-Cd complex keeps stable at this rotating speed. When $V_m$ increases to 10.0 L, the content of residual copper in the retentate is very little, and the separation of Cu (II) and Cd (II) is achieved.

![Figure 5: Variation of $C_{Cu}$ and $C_{Cd}$ with $V_m$](image)

After Cu (II) was removed, the rotating speed increased to 2000 rpm, PAA-Cd complex would dissociate and the dissociated Cd (II) was collected in permeate, the PAAS remained in the retentate, as shown in Figure 6. The concentration of Cd (II) in the retentate decreases as the addition of make-up water, the PAA-Cd complex is completely dissociated when $V_m$ reaches 7.0 L, and the PAAS is regenerated.

![Figure 6: Variation of $C_{Cd}$ with $V_m$](image)

4 CONCLUSIONS

Selective separation of Cu (II) and Cd (II) from aqueous solution by shear induced dissociation and ultrafiltration have been investigated using rotating disk membrane and PAAS as complexing agent. At pH 6, P/M 27.5, the separation of Cu (II) and Cd (II) has been achieved at 1300 rpm from simulated aqueous solution, and the regeneration of PAAS has been finished at 2000 rpm from polymer-metal complex solution. Compared with acidification, shear induced dissociation, is a novel and green technology for recovery of heavy metal ions and polymer from aqueous solutions without the consumption of acid and alkali.

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