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Selective separation of Cd(II), Zn(II) and Pb(II) from Pb-Zn smelter wastewater via shear induced dissociation coupling with ultrafiltration

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Abstract−Treatment of Pb-Zn smelter wastewater via complexation-ultrafiltration (C-UF) was studied using copolymer of acrylic acid-maleic acid (PMA) as complexant. The complexing reaction kinetics of M (Cd(II), Pb(II) and Zn(II)) with PMA were examined for the first time and the pseudo-first-order model could be employed to simulate the reaction. The effects of the mass ratio of PMA to metal ions (P/M) and pH on the simultaneous removal of Cd(II), Zn(II) and Pb(II) via C-UF were investigated, and the optimized P/M and pH are 10 and 7.0, respectively. Furthermore, the shear stability of PMA-Cd, PMA-Zn and PMA-Pb complexes was investigated, and the corresponding critical shear rates (γ_c), the smallest shear rate at which the complexes begin to dissociate were 1.98×10^5, 1.81×10^4 and 1.38×10^5 s^{-1}, respectively. The selective recovery of Cd(II), Zn(II) and Pb(II) from Pb-Zn Smelter wastewater as well as the regeneration of PMA were fulfilled by shear induced dissociation coupled with ultrafiltration (SID-UF) according to the difference of critical shear rates of PMA-M complexes, and the regenerated PMA showed almost the same complexation ability as the original.

Keywords: Wastewater Treatment, Selective Separation, Complexation-ultrafiltration, Critical Shear Rate, Shear Induced Dissociation

INTRODUCTION

Heavy metal contamination in aqueous effluents originates from industrial and agricultural activities [1,2]. Wastewater containing cadmium, lead and zinc is mostly produced in the Pb-Zn smelter and mining industry [3,4]. These metals can accumulate in the environment owing to their durability and non-biodegradability, which may pose a major threat to human health and ecological systems [5-8]. Therefore, it is essential to explore efficient, environment-friendly methods to remove and separate them from effluent.

Up to now, various chemical and physicochemical technologies for the treatment of heavy metals contaminated wastewaters have been exploited, such as biosorption, ion exchange, chemical flocculation, adsorption, chemical precipitation, membrane process and extraction [9-14]. Among these, chemical precipitation is one of the most commonly methods used and is considered as the most economical [15,16]. However, it is incapable of depressing the heavy metal from wastewater up to the desirable minimum concentration [17,18]. Adsorption, membrane process and ion-exchange have been considered as promising ways to remove the metal ions in low concentration effluent, but these technologies show complicated conditions and high economic cost in industrial application. Although extraction can achieve selective separation, most of the reagents produced by this process are harmful to the environment [10]. Hence, an effective alternative is being searched for to replace or supplement conventional processes of heavy metals removal from industrial wastewater.

During recent years, owing to high removal efficiency and low energy requirement, complexation-ultrafiltration (C-UF) has been found to be effective for the treatment of metal ions from effluents [19,20]. The principle of C-UF is that complexing agent and heavy metal ions can interact to generate complexes, which can be retained by ultrafiltration membranes to achieve the purpose of metal removal [21-23]. It has been successfully applied for removing Co^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, Cu^{2+}, W^{6+}, Sn^{2+} and other heavy metal ions [24-28]. For conventional C-UF, the recovery of the metals and complexing agents is achieved by acidification dissociation since the sensitivity of pH on the formation of polymer-metal complexes varies from metal to metal [20,29]. However, this method not only consumes a great amount of alkali and acid, but also it cannot separate metals effectively.

Herein, a novel separation technique that can overcome disadvantages of conventional acidification method was proposed, called shear induced dissociation coupled with ultrafiltration technology (SID-UF). SID-UF consists of two steps: multicomponent metal ions are first bound with complexant to form polymer-meal complexes which can be rejected by C-UF; then, according to the difference of shear stability of polymer-metal complexes, selective separation of metals can be fulfilled by shear induced dissociation coupled with ultrafiltration [30]. In comparison to conventional separation methods, such as acidification and extraction, SID-UF avoids the production of harmful reagents and decreases the consumption of alkali and acid. Moreover, it shows excellent separation efficiency for metal ions, and the regenerated complexant has good complexing performance [31]; thus, it is environmentally friendly and efficient for selective recovery of metals from wastewater. In our previous studies, SID-UF was used to effectively separate Zn(II) and Cu(II) in electroplating wastewater using PAAS (polyacrylic

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acid sodium) as complexant [30]. Additionally, PMA (copolymer of acrylic acid-maleic acid) with high content of carboxylic has been effectively employed to treat heavy metal ions by C-UF [28]. However, to date, the treatment for Pb-Zn smelter wastewater via SID-UF using PMA as complexing agent has not been reported.

This work describes the treatment of Pb-Zn smelter wastewater by C-UF using PMA as complexing agent. The complexation reaction kinetics of M with PMA was explored for the first time. And then, the effects of P/M and pH on the simultaneous removal of M via C-UF were investigated. The shear stability of PMA-M complexes was studied using rotation disk membrane (RDM) and the critical shear rates of PMA-M complexes were obtained. Finally, SID-UF was conducted to selectively separate Cd(II), Zn(II) and Pb(II) and regenerate PMA from Pb-Zn smelter wastewater according to the difference of γ_c of PMA-M complexes.

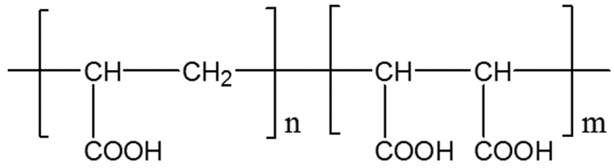

Fig. 1. Structure of the PMA.

EXPERIMENTAL

1. Material and Apparatus

PMA (average molecular weight is 70 kDa) was used as complexant and its structure is shown in Fig. 1. $ZnSO_4 \cdot 7H_2O$, $Pb(NO_3)_2$, $Cd(NO_3)_2 \cdot 4H_2O$ were used to prepare simulated solution. Either HCl (0.1 mol) or NaOH (0.1 mol) was served to change pH. The original PMA were pretreated to remove the smaller fractions by diafiltration [32]. Pure water was applied in the experiments. The PES (polyether sulfone) flat ultrafiltration membrane with MWCO (molecular weight cut-off) 20 kDa was used. The Pb-Zn Smelter wastewater was employed in this study and the real wastewater samples were obtained from a Pb-Zn smelter in Zhuzhou, China. The initial metal ions composition of the real wastewater samples are listed in Table 1.

The experimental device (RDM module) is displayed in Fig. 2. A circular disk is installed inside a 0.088 m inner radius cylindrical housing. Fig. 2 illustrates the diagram of a circular disk with six radial vanes. The other end of the shaft outside the housing is connected to an electromotor that can drive the disk to rotate. The motor can provide a speed of 0-3,000 rpm for the rotating disk. A flat PES ultrafiltration membrane (effective area is 0.0253 m^2) is installed on the bottom of housing cavity. The axial distance between disk and membrane is 14 mm. A cooling water circulation system is installed in the bearing for cooling the driving shaft and maintaining a constant fluid temperature in the housing cavity [28]. The permeate outlet is located at the 0.059 m from center of behind plate, and retentate flows from the center of behind plate. The feed inlet is located on the upper plate of housing cavity.

Table 1. The concentration of heavy metal ions in real wastewater samples at different stages

Parameters	Initial composition	After precipitation	After complexation-ultrafiltration
Final pH	3.0±0.2	7.0	7.0
Pb(II) (mg L^{-1})	81.2±0.3	73.2	<0.1
Cd(II) (mg L^{-1})	163.2±0.6	135.4	<0.1
Zn(II) (mg L^{-1})	256.2±0.3	89.1	<0.1
Al(III) (mg L^{-1})	17.6±0.5	<0.1	-
Fe(III) (mg L^{-1})	35.3±0.3	<0.1	-

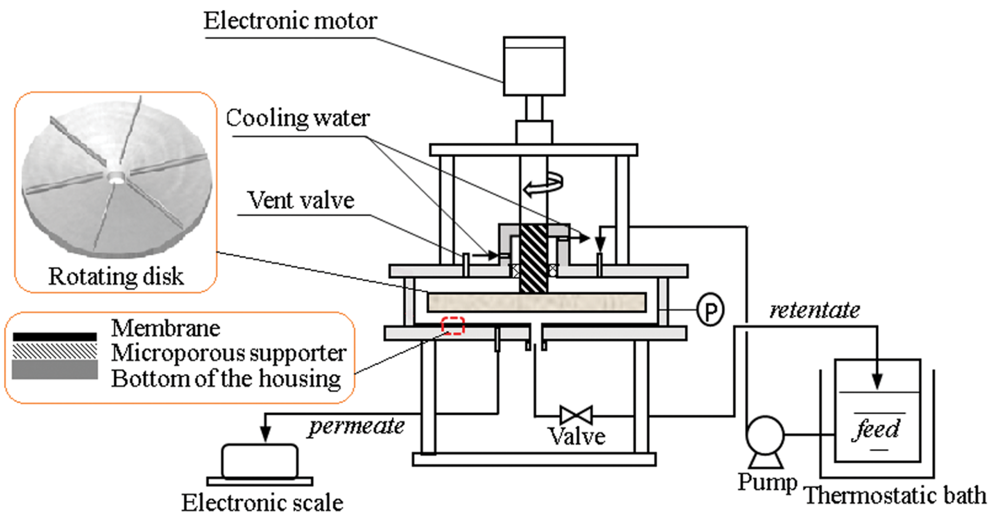

Fig. 2. Schematic of experimental set-up.

2. UF Experiment

The UF experiments were conducted in the recirculation reflux process. The mixture solution of PMA with simulated ternary metal ions solution or pretreated real wastewater was 2 L. After adjusting the solution pH and P/M to a desired value, the mixed solution was thoroughly stirred for 2 h. A series of solution pHs (ranging from 3 to 8), P/Ms (ranging from 2 to 10) and disk rotation speeds (ranging from 0 to 3,000 rpm) were independently increased to investigate their effects on rejection. The retentate was sent back to the feed bath, and the permeate was collected in a beaker. All UF tests are guaranteed at room temperature. The concentration of metal ions and the concentration of PMA were measured by ICP-OES (Optima 8000, Perkin Elmer, USA) and TOC (TOC-DCSH, Japan), respectively. The pH value was gauged by a digital display pH meter (PHS-25, China).

3. SID-UF Experiment

The SID-UF process consists of four steps: first, the metal ions were bound with PMA to form PMA-M complexes and could be rejected by ultrafiltration membrane, thereby achieving the purpose of removing heavy metal ions; then, Zn(II) could be separated from the concentrated PMA-M complexes solution by controlling appropriate shear rate ($\gamma_{c(PMA\text{-}Zn)}<\gamma<\gamma_{c(PMA\text{-}Pb)}$) according to the difference of critical shear rates (γ_c) of PMA-Zn and PMA-Pb complexes, PMA-Zn complex will dissociate, and free Zn(II) will pass through the membrane. After all the zinc ions were dissociated and separated, the rotation speed was increased to a shear rate between $\gamma_{c(PMA\text{-}Pb)}$ and $\gamma_{c(PMA\text{-}Cd)}$, so that PMA-Pb complex dissociated and lead ions were separated by ultrafiltration. In the same way, the separation of Cd(II) and the regeneration of PMA were fulfilled at a higher critical shear rate greater than $\gamma_{c(PMA\text{-}Cd)}$. A certain amount of pure water was continuously and simultaneously added to the feed tank to keep the volume of the feed constant throughout the SID-UF process. The permeation coefficient (F), permeate flux per unit trans-membrane pressure, stayed at about 1.35×10^{-8} m Pa^{-1} s^{-1} in this study. The Pb-Zn smelter wastewater was pretreated by chemical precipitate before this experiment.

4. Pretreatment of Pb-Zn Smelter Wastewater by Chemical Precipitate

Initial ICP results on the real wastewater collected from a Pb-Zn smelter in Zhuzhou, China, indicate that the major metal contaminants were Cd(II), Pb(II) and Zn(II) (Table 1). Other contaminants included Al(III) and Fe(III). The pH of wastewater was analyzed by a digital display pH meter and the average pH of wastewater was 3.0±0.2. For these metals, chemical precipitation (at pH 7.0) is capable of reducing the concentrations directly from the primary discharge site to below 0.1 mg/L for Fe(III) and to below 0.1 mg/L for Al(III), while the concentration of Cd(II), Pb(II) and Zn(II) are 135.4, 73.2 and 89.1 mg/L, respectively (Table 1). The pretreated wastewater was used in all subsequent experiments.

RESULTS AND DISCUSSION

1. Formation Kinetics of PMA-M Complexes

The pretreated wastewater was added to the 2 L reservoir in advance; then, sufficient PMA was introduced to the wastewater. The mixture pH was adjusted to 7.0. The retentate and permeate stream were simultaneously added to the feed tank to keep the volume of the feed constant. This experiment was carried out at 25 °C. When the reactions started, variations of the metal ions concentrations of the permeate with times were determined. The kinetic curves of the PMA-M complexes formation are illustrated in Fig. 3. C_f is initial feed concentration and C_p is the permeate concentration. C_M is C_p/C_f. The results show that the C_M decreases with the complexation time and attains nearly 0 and does not change again. The complexation equilibrium time of PMA for metal ions decreases in the sequence Zn(II)>Pb(II)>Cd(II).

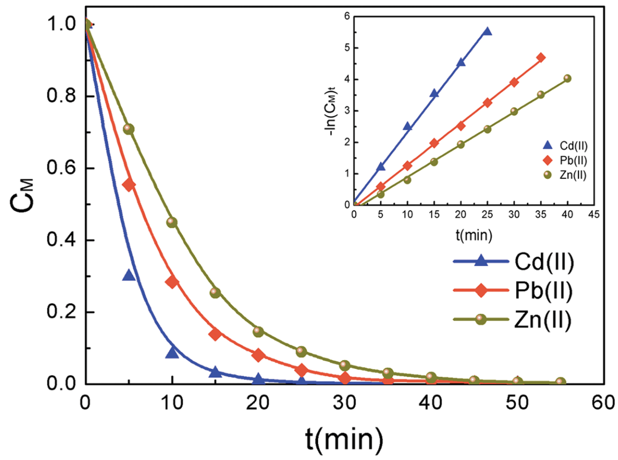

Fig. 3. Kinetic curves for the formation of PMA-Cd, PMA-Zn and PMA-Pb complexes, respectively (pH, 7.0; P/M, 35; temperature, 25 °C; transmembrane pressure, 10 kPa).

Since the formation rate of the PMA-M complexes is related to the concentration of PMA, M and H^+, the differential equation of complexation reaction rate can be expressed by Eq. (1) according to definition of chemical reaction rate and chemical kinetic theory [21,33]:

$$-\frac{dC_M}{dt}=K(C_M)^d(C_{H^+})^e(C_{PMA})^f \quad (1)$$

where K is the constant of reaction rate; t is the reaction time; d, e and f are the orders of reaction.

Under a constant pH and excess PMA, the equation of reaction rate is as follows:

$$-\frac{dC_M}{dt}=K^*(C_M)^d \quad (2)$$

where K^* is the constant of observed rate; assuming d=1, the differential equation of complexation reaction rate can be converted as follows [21]:

$$-\frac{dC_M}{dt}=K_1C_M \quad (3)$$

where K_1 is the constant of pseudo-first-order rate. Eq. (3) is integrated, taking t=0 to t and $C_M=(C_M)_0$ to $(C_M)_t$ into consideration, the kinetic equation can be derived as Eq. (4):

$$-\ln(C_M)_t=K_1t-\ln(C_M)_0 \quad (4)$$

The correlation of $-\ln(C_M)_t$ vs t was fitted on the basis of linear

Table 2. Kinetic parameters of the complexation reactions of PMA with M (Zn(II), Pb(II) and Cd(II))

Metal ions	k_1 (min^{-1})	$-\ln(C_M)_0$	Regression coefficient (R^2)
Zn(II)	0.103	−0.136	0.998
Pb(II)	0.133	−0.059	0.999
Cd(II)	0.219	0.126	0.996

fitting, as presented in Fig. 3. The $-\ln(C_M)_t$ and t showed a good linear correlation, suggesting that the kinetics equation of pseudo-first-order could be applied to simulate the reaction of M with PMA at 25 °C. The kinetic parameters of complexation reaction are tabulated in Table 2. This study can provide guidance for the complexation time of the following experiments.

2. Simultaneous Removal of Cd(II), Zn(II) and Pb(II) in Pb-Zn Smelter Wastewater by C-UF

pH has a critical effect on the removal of metal ions by C-UF owing to the mechanism of competitive complexation between metal ions and hydrogen ions [34,35]. The influence of pH on the removal of Cd(II), Pb(II) and Zn(II) was explored using pre-treated wastewater. Fig. 4(a) displays effects of pH on the rejections in ternary metal ions solution at P/M 8. The rejection of cadmium is nearly 100% at pH 5.5, whereas less than 60% for both of lead and zinc. It gives direct evidence that PMA has a higher affinity with cadmium. When the solution pH was raised from 5.5 to 7.0, the lead removal rate approached 100%, which can be attributed to the fact that a greater amount of deprotonated carboxylic groups on PMA chains at higher pH has a higher bonding capacity between PMA and metals [36]. When pH was further increased from 7.0 to 8.0, zinc ions still could not be removed completely, because there were not enough carboxylic groups to complex metal ions at P/M 8. This study demonstrates that the order of affinity of the complexation reaction of M with PMA is Cd(II)>Pb(II)>Zn(II), which agrees with previous study [37,38].

To remove Cd(II), Pb(II) and Zn(II) completely and ensure the effective utilization of PMA, the influence of P/M on the simultaneous removal of Cd(II), Pb(II) and Zn(II) was examined using pre-treated wastewater. The neutral condition (pH, 7.0) was used in this work to avoid formation of hydroxides at slightly alkaline pH values [21,39]. The results are presented in Fig. 4(b). Note that the rejection of cadmium quickly reaches nearly 100% as the P/M is increased from 0 to 6, while the removal rate of zinc is less than 70%, because metal ions with stronger binding ability are preferentially bound with binding sites in PMA [39]. With the increase of PMA, lead and zinc with relatively low binding ability begin to bind with polymers, and the rejection of lead and zinc also gradually increases. The removal rate of cadmium, zinc and lead approaches 100% at P/M ≥10, indicating that free heavy metal ions in the wastewater are all bound by complexant. Considered from the economical cost of PMA and the removal rate of metal ions, the optimized conditions are P/M 10 and pH 7.0 for simultaneous removal of Cd(II), Pb(II) and Zn(II) by C-UF.

3. The Shear Stability of PMA-Cd, PMA-Zn and PMA-Pb Complexes

Previous studies showed that the PAA-metal complexes can be dissociated when the shear rate (γ) is greater than the critical shear rate (γ_c) of the polymer-metal complexes [31,40]. Based on the above finding, it is conceivable that the PMA-M complexes will dissociate at $\gamma \geq \gamma_{c(PMA-M)}$. Thus, this study was aimed at investigating the shear stabilities of PMA-M complexes to guide the following SID-UF experiments.

3-1. Variation of Shear Rate Distribution on the Membrane with Rotation Speed

Since the shear rate γ was difficult to measure by conventional methods, the computational fuid dynamics (CFD) software was applied to simulate the shear rate distribution on RDM surface. The distribution of γ along the membrane radius at different disk rotation speeds (N) is shown in Fig. 5. Within the region of radius 0.08 m, shear rate increases with the radius at the same N. Additionally, higher rotation speed induces greater shear rate. This results is coincident with the results of previous studies [41,42]. Based on the boundary layer theory, when the fluid flows near the solid wall, the fluid velocity near the wall of the RDM housing is decelerated due to the resistance of the wall. Thus, the shear rate close to the membrane periphery (r=0.088 m) has a slight deviation from the original uptrend and decreases a little; this conclusion has also been

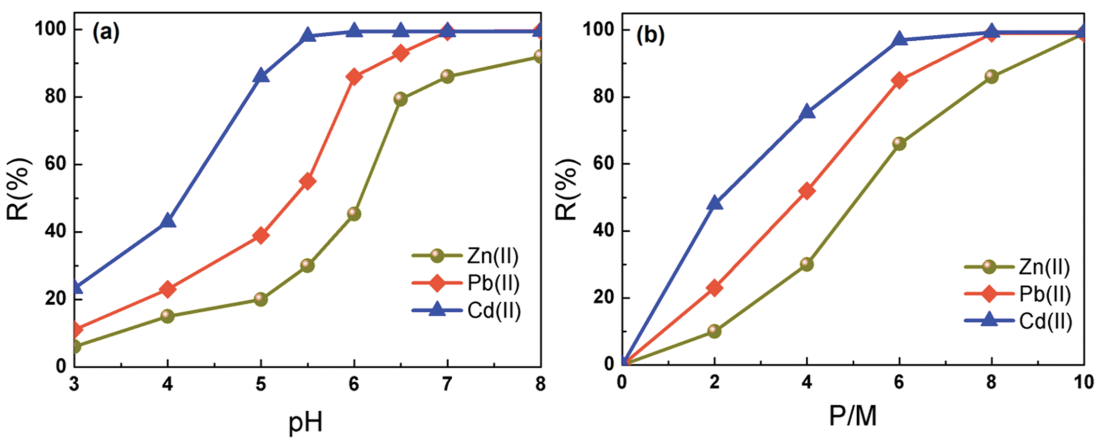

Fig. 4. (a) Effect of pH on the rejections of metal ions at P/M 8; (b) Effect of P/M on the rejections of metal ions at pH 7.0. (temperature, 25 °C; initial pressure, 10 kPa).

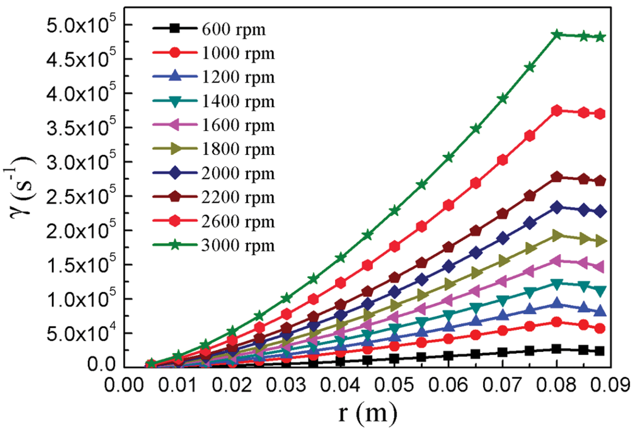

Fig. 5. CFD calculations of distribution of the shear rate on the membrane surface at different rotating speeds.

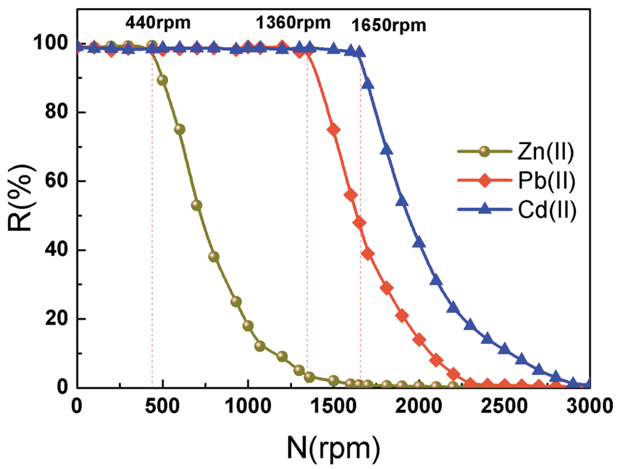

Fig. 6. Effect of rotating speed on the rejection of metal ions in pretreated real wastewater (b) the critical shear radius of PMA-M complex (pH, 7.0; P/M 10; temperature, 25 °C; initial pressure, 10 kPa).

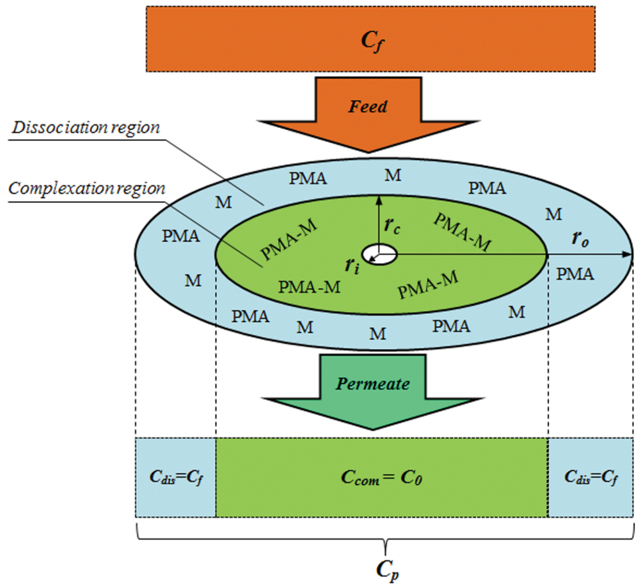

Fig. 7. The distribution of the form of metals on the membrane surface in the shear field (Inorganic anions and sodium omitted).

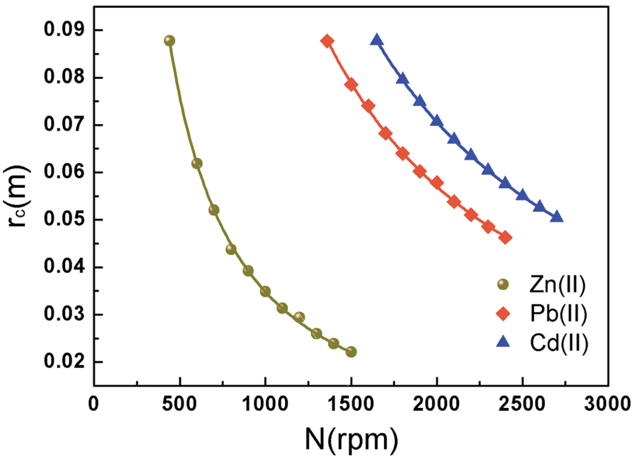

Fig. 8. Effect of rotating speed on the critical shear radius of PMA-M complex (pH, 7.0; P/M 10; temperature, 25 °C; initial pressure, 10 kPa).

proved by Zhang et al. [31].

3-2. The Critical Radius and Critical Shear Rate of PMA-M Complexes

The shear stability of PMA-M complexes was investigated by RDM module using pretreated real wastewater. The rejection of metal ions varied with N at P/M 10 and pH 7.0 as displayed in Fig. 6. It is interesting that the rejection of metal ions decreases once N exceeds a critical value, and gradually reduces with the improvement of speed. This fact can be explained as follows: the PMA-M complexes start to dissociate when N exceeds the critical rotation speed N_c (the smallest disk rotation speed at which complexes start to dissociate) and the dissociation region gets larger from membrane periphery to membrane center with the increase of N, resulting in the sustained decrease of metal ions removal rate [31]. As can be seen in Fig. 6, the N_c of PMA-Cd, PMA-Pb and PMA-Zn complexes is 1,650, 1,360 and 440 rpm at pH 7.0, respectively.

According to Fig. 6, it is conceivable that at a certain N, the PMA-M complexes near the center of the membrane will remain stable even if the complexes near the edge of the membrane have dissociated. Thus, the distribution of PMA-M complexes on the membrane surface can be revealed with the help of the segmentation model [40], as shown in Fig. 7, where r_i is the membrane inside radius (0.005 m), r_o is the membrane outer radius (0.088 m). The critical radius (r_c) is defined as the minimum ring radius where dissociation of PMA-M occurs [31]. PMA-M are entirely dissociated in dissociation region ($r_c \le r \le r_o$), and the permeate concentration (C_{dis}) can be counted as the initial concentration of raw material solution (C_f). PMA-M complex is stable in complexation region ($r_i \le r < r_c$), and the permeate concentration (C_{com}) can be regarded as metal ion concentration of permeate in C-UF process (C_0). The calculation equation of r_c was discussed in our previous study and can be simplified as below [40]:

Table 3. γ_c **of PMA-M complexes and correlations of** r_c **and N at pH 7.0**

Complexes	N_c (rpm)	γ_c (s^{-1})	Fitting equation	Regression coefficient (R^2)
PMA-Zn	440	1.81×10^4	$r_c=82N^{-1.125}$ (N≥440)	0.998
PMA-Pb	1,360	1.38×10^5	$r_c=294N^{-1.125}$ (N≥1360)	0.998
PMA-Cd	1,650	1.96×10^5	$r_c=366N^{-1.125}$ (N≥1650)	0.999

$$r_c^4+\frac{364P_0}{\rho k^2N^2}r_c^2+\frac{C_p-C_{dis}}{C_{dis}-C_{com}}\left(r_i^4+\frac{364P_0}{\rho k^2N^2}r_i^2\right)+\frac{C_{com}-C_p}{C_{dis}-C_{com}}\left(r_o^4+\frac{364P_0}{\rho k^2N^2}r_o^2\right)=0 \quad (5)$$

where ρ represents the solution density (kg·m^{-3}), P_0 is the pressure at the membrane center, k is the velocity following factor and the value is 0.796 in this study [40]. Fig. 8 illustrates the fitting curve of r_c of PMA-M complexes calculated by Eq. (5), and the fitted relationship of r_c and N is shown in Table 3. The r_c decreased with the increasing of N, indicating that a larger N ensures a greater dissociation region. This conclusion qualified the better segmentation model on the membrane surface. To further investigate the stability of the PMA-M complexes in shear field, the γ_c of the PMA-M complexes were calculated according to the empirical formulas of Bouzerar et al. [41]. The formulas are as follows:

$$\gamma_{cl}=0.026\upsilon^{-0.5}(kN_c)^{1.5}r_c \quad (6a)$$

$$\gamma_{ct}=0.0005\upsilon^{-0.8}(kN_c)^{1.8}r_c^{1.6} \quad (6b)$$

where γ_{ct} and γ_{cl} are the critical shear rates of PMA-M complexes in turbulent (N_c>570 rpm) and laminar (N_c≤570 rpm) flow, respectively. υ is kinematic viscosity of treated fluid (m^2 s^{-1}). The γ_c of the PMA-M complexes are shown in Table 3. At pH 7.0, the γ_c of PMA-Cd, PMA-Pb and PMA-Zn complexes is 1.98×10^5, 1.38×10^5 and 1.81×10^4 s^{-1}, respectively. The result indicates that the sequence of the shear stability of the complex is PMA-Cd>PMA-Pb>PMA-Zn under the pH 7.0.

4. The Optimized Conditions of Selective Separation

On the basis of Section 3.2, PMA-M complexes can be dissociated when γ exceeds γ_c, so we can utilize this to selectively separate heavy metals using SID-UF based on the difference of γ_c of PMA-M complexes. The selective separation factors ($\beta_{Zn/Pb}$, $\beta_{Pb/Cd}$, $\beta_{Zn/Cd}$) of the both metals are introduced for quantitatively describing the separation, and the higher β value ensures the greater separation performance of different metals [31,43]. The formula of β is universally defined as follows:

$$\beta_{Zn/Pb}=\frac{1-R_{Zn}}{1-R_{Pb}} \quad (7a)$$

$$\beta_{Pb/Cd}=\frac{1-R_{Pb}}{1-R_{Cd}} \quad (7b)$$

$$\beta_{Zn/Cd}=\frac{1-R_{Zn}}{1-R_{Cd}} \quad (7c)$$

where R_{Cd}, R_{Pb} and R_{Zn} are the rejection rates of Cd(II), Pb(II) and Zn(II), respectively. Since the rotation speed N can significantly affect the removal rate of metal ions, the variation of $\beta_{Zn/Pb}$, $\beta_{Pb/Cd}$ and $\beta_{Zn/Cd}$ with N (from 0 to 3,000 rpm) was explored using pre-treated real wastewater at pH 7.0 and P/M 10, as it is presented in Fig. 9. As N increases, β constantly maintains nearly 1 first, then it sharply rises to a peak value and finally drops to1. This could be interpreted as follows: at low N, the γ provided by rotating disk is less than the γ_c of three complexes, making the high rejections of all metal ions and low β. When N attains the N_c of the complex with lower shear stability, the rejection of the corresponding metal ion decreases, which results in the value of β representing an enlargement tendency. With the continuous increase of N, γ exceeds the γ_c of complex with relatively higher stability, the rejection of another metal ion also begins to decrease, causing the sharp reduction of β. This result can be inferred that selective separation of Cd(II), Zn(II) and Pb(II) can be achieved by selecting an appropriate rotation speed. As can be seen in Fig. 9, the maximum $\beta_{Zn/Pb}$, $\beta_{Pb/Cd}$ and $\beta_{Zn/Cd}$ are obtained at 960, 1550 and 960 rpm at pH 7.0, respectively. And the related γ are calculated to 7.39×10^4, 1.75×10^5 and 7.39×10^4 s^{-1}, respectively. The experimental data provides guidance for the SID-UF experiment.

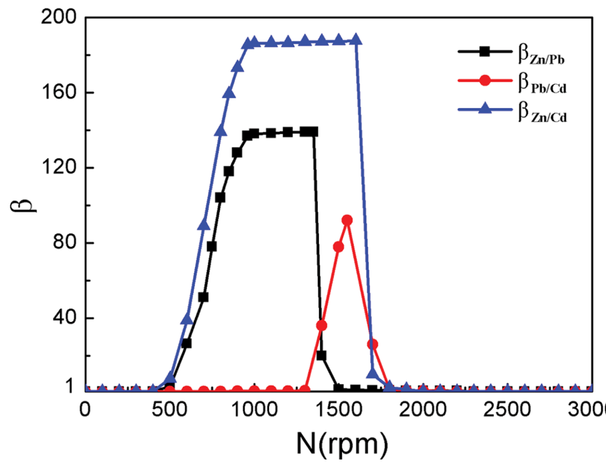

Fig. 9. Effect of rotating speeds on selective separation coefficient β at optimal pH 7.0.

5. Selective Recovery of Cd(II), Zn(II), Pb(II) and Regeneration of PMA

The pre-treated Pb-Zn smelter wastewater was mixed with the PMA to form PMA-M complexes solution at conditions of P/M 10 and pH 7.0. Then, SID-UF was conducted to selectively recover Cd(II), Zn(II) and Pb(II) as well as regenerate PMA from concentrated PMA-M complexes solution, and the results are illustrated in Fig. 10, where V_R is the volume ratio of make-up deionized water to initial feed, C_R denotes the concentration ratio of retentate to the initial feed. In a shear field at 960 rpm (7.39×10^4 s^{-1}), because the γ is greater than the γ_c of PMA-Zn complex (1.81×10^4 s^{-1}) but less than those of PMA-Pb complex (1.38×10^5 s^{-1}), PMA-Pb complex can remain stable, while PMA-Zn complex will dissociate, and

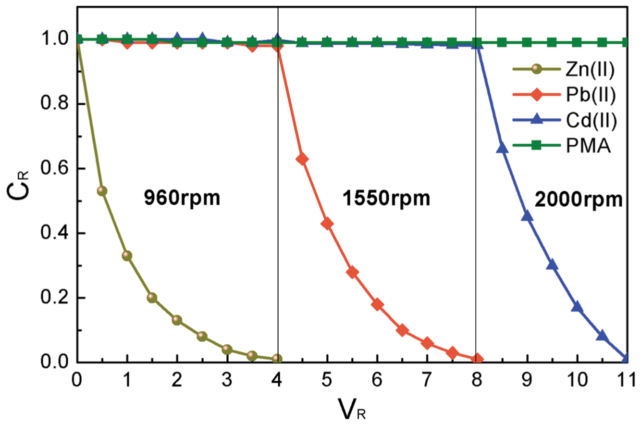

Fig. 10. Effect of V_R on C_R of metal ions and PMA (pH, 7.0; P/M 10; temperature, 25 °C; initial pressure, 10 kPa).

the free zinc ions will permeate through the membrane. Therefore, the content of residual Zn(II) decreases obviously, while the concentrations of Cd(II) and Pb(II) remain constant, as displayed in Fig. 10. When V_R=4.0, the zinc ions are almost completely recovered in permeate. Similarly, the rotation speed was adjusted to 1,550 rpm (1.75×10^5 s^{-1}); when V_R=8.0, Pb(II) would almost entirely enter the permeate. Having achieved the recovery of Pb(II) and Zn(II), PMA was regenerated at $N>N_{c(Cd(II))}$ (2,000 rpm, $\gamma=2.76\times10^5$ s^{-1}). As illustrated in Fig. 10, when the V_R reaches 11.0, the C_R of Cd(II) drops to almost 0, while the C_R of PMA stays constant and approaches 1, meaning that PMA is regenerated and Cd(II) is recovered successfully.

Further, the regenerated PMA and original PMA were used to remove Zn(II) at the optimum conditions [36]. The simulated solution of 10 mg/L Zn(II) was used in this experiment. The effect of PMA regeneration times on the removal of Zn(II) is shown in Fig. 11. The PMA was regenerated 15 times, which still guaranteed a removal rate of 97.5% for Zn(II). The slightly low rejection of Zn(II) of regenerated PMA than that of original PMA was expected, which is ascribed to the fact that if the N of PMA regeneration is 2,000

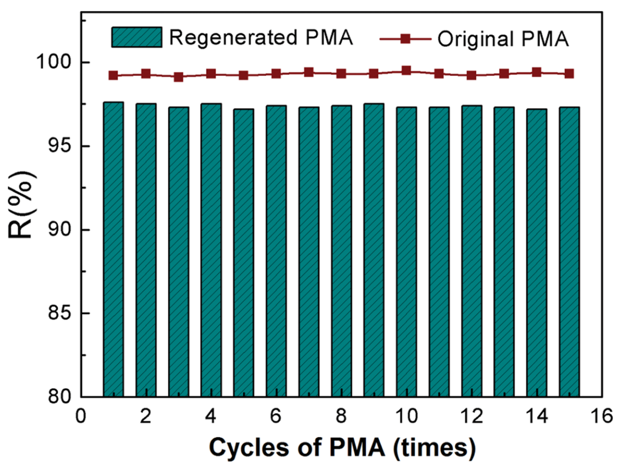

Fig. 11. Variations of the rejection of Zn(II) with different times of PMA cycles (pH 7.0; P/M 8; initial metal ion concentrations, 10 mg L^{-1}; temperature, 25 °C; initial pressure, 10 kPa).

rpm, there exists a small part of complexing region on the membrane surface as shown in Fig. 8, which makes very little PMA-M complexes present in the regenerated PMA. Thus the real content of PMA in the regenerated solution was slightly lower than that of original PMA at the same P/M [40]. This result demonstrated that PMA can be effectively regenerated by SID-UF and the regenerated PMA showed almost the same complexation ability as the original.

CONCLUSIONS

Treatment of Pb-Zn smelter wastewater containing M (Cd(II), Zn(II) and Pb(II)) by complexation-ultrafiltration was studied using copolymer of acrylic acid-maleic acid (PMA) as complexant and the optimal conditions were P/M 10 and pH 7.0. The complexing reaction kinetics of heavy metal ions with PMA was examined, which showed that the complexation equilibrium time of PMA for metals decreased in the sequence Zn(II)>Pb(II)>Cd(II), and the pseudo-first-order model could be employed to simulate the reaction. Furthermore, the shear stability of PMA-M complexes was studied. It was proved that the sequence of the shear stability of the complex is PMA-Cd>PMA-Pb>PMA-Zn at the same pH. Most importantly, this study provides a novel and efficient technology, shear induced dissociation coupling with ultrafiltration (SID-UF), for the removal and selective separation of Cd(II), Pb(II) and Zn(II) and regeneration of the complexant from Pb-Zn smelter wastewater according to the difference of shear stability of the three PMA-M complexes. In comparison to conventional separation methods, such as acidification and extraction, SID-UF avoids the production of harmful reagents and decreases the consumption of alkali and acid. SID-UF exhibits a promising potential for treatment of metals from effluent.

NOMENCLATURE

Roman Letters

C_0 : metal concentration of the permeate at rest [mg L^{-1}]
C_f : metal concentration of the feed [mg L^{-1}]
C_{H^+} : H^+ concentration [mg L^{-1}]
C_M : metal concentration ratio of the permeate to the initial feed
C_{PMA} : PMA concentration [mg L^{-1}]
C_p : metal concentration of the permeate [mg L^{-1}]
C_R : metal concentration ratio of retentate to the initial feed
C_{com} : metal concentration of the permeate through the complexation region [mg L^{-1}]
C_{dis} : metal concentration of the permeate through the dissociation region [mg L^{-1}]
F : permeation coefficient [L m^{-2} kPa^{-1} h^{-1}, m s^{-1} Pa^{-1}]
K : rate constant
K_1 : pseudo-first-order rate constant
K* : observed rate constant
k : velocity following factor
N : rotation speed [rpm]
N_c : critical rotation speed [rpm]
P_0 : center pressure [kPa]
r_0 : membrane outsider radius [m]

r_i : membrane insider radius [m]
r_c : critical radius [m]
R : rejection of metal [%]
R^2 : regression coefficient
t : time [s]
V_R : the volume ratio of supplementary deionized water to the initial feed

Greek Letters

ν : kinematic viscosity [m^2s^{-1}]
ρ : fluid density [kg m^{-3}]
γ : shear rate [s^{-1}]
γ_c : critical shear rate [s^{-1}]
γ_{cl}, γ_{ct} : critical shear rate on membrane surface in the laminar regime and turbulent regime [s^{-1}]
β : selective separation factor

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REFERENCES

1. D. Vilela, J. Parmar, Y. Zeng, Y. Zhao and S. Sánchez, *Nano Lett.*, **16**, 2860 (2016).
2. A. G. Alejandro, H. M. Virginia, B. P. Adrian, M. A. Montes and D. I. Mendoza, *Ind. Eng. Chem. Res.*, **50**, 9354 (2011).
3. E. Kim, L. Horckmans, J. Spooren, K. C. Vrancken, M. Quaghebeur and K. Broos, *Hydrometallurgy*, **169**, 372 (2017).
4. Q. Zhang, B. Pan, W. Zhang, B. Pan, L. Lv, X. Wang, J. Wu and X. Tao, *J. Hazard. Mater.*, **170**, 824 (2009).
5. A. Heidari, H. Younesi and Z. Mehraban, *Chem. Eng. J.*, **153**, 70 (2009).
6. M. G. Kiran, K. Pakshirajan and G. Das, *Chem. Eng. J.*, **321**, 67 (2017).
7. A. Concas, S. Montinaro, M. Pisu and G. Cao, *Chem. Eng. Sci.*, **62**, 5186 (2007).
8. A. Rahmani, H. Z. Mousavi and M. Fazli, *Desalination*, **253**, 94 (2010).
9. Y. Liu, Q. Peng, Y. Yang, Y. Bo, Y. Wang, S. Ye and Y. Chen, *J. Environ. Sci. (China)*, **67**, 227 (2018).
10. I. K. Moideen, A. M. Isloor, A. A. Qaiser, A. F. Ismail and M. S. Abdullah, *Korean J. Chem. Eng.*, **35**, 1 (2018).
11. S. Anbalagan, S. K. Ponnusamy, S. R. P. Selvam, A. Sankaranarayan and A. Dutta, *Korean J. Chem. Eng.*, **33**, 2716 (2016).
12. J. Wang, Y. Zhao, P. Zhang, L. Yang, H. A. Xu and G. Xi, *Chin. J. Chem. Eng.*, **22**, 231 (2018).
13. S. Habibi, A. Nematollahzadeh and S. A. Mousavi, *Chem. Eng. J.*, **267**, 306 (2015).
14. A. Nematollahzadeh, S. Seraj and B. Mirzayi, *Chem. Eng. J.*, **277**, 21 (2015).
15. X. Z. Li, Q. L. Zhao and X. D. Hao, *Waste Manage.*, **19**, 409 (2014).
16. J. F. Zhang, T. E. Brutus, J. M. Cheng and X. G. Meng, *J. Environ. Sci. (China)*, **57**, 190 (2017).
17. Y. Zheng and A. Wang, *Chem. Eng. J.*, **162**, 186 (2010).
18. N. Meunier, P. Drogui, C. Montané, R. Hausler, G. Mercier and J. F. Blais, *J. Hazard. Mater.*, **137**, 581 (2006).
19. C. W. Li, C. H. Cheng, K. H. Choo and W. S. Yen, *Chemosphere*, **72**, 630 (2008).
20. M. A. Barakat and E. Schmidt, *Desalination*, **256**, 90 (2010).
21. J. X. Zeng, H. Q. Ye and Z. Y. Hu, *J. Hazard. Mater.*, **161**, 1491 (2009).
22. A. Y. Jiao, Z. S. Li and L. C. Bao, *Desalination*, **322**, 29 (2013).
23. K. Evina, M. Simos and K. J. Haralambous, *Chemosphere*, **82**, 557 (2011).
24. Y. Huang, D. Wu, X. Wang, W. Huang, D. Lawless and X. Feng, *Sep. Purif. Technol.*, **158**, 124 (2016).
25. G. Borbély and E. Nagy, *Desalination*, **240**, 218 (2009).
26. M. A. Khosa, S. S. Shah and X. Feng, *Chem. Eng. J.*, **244**, 446 (2014).
27. L. Javier, P. Angel, M. A. Rodrigo and C. I. Pablo, *J. Hazard. Mater.*, **168**, 25 (2009).
28. H. S. Le, Y. R. Qiu and S. Y. Tang, *Desal. Water Treat.*, **160**, 41 (2019).
29. R. Camarillo, Á. Pérez, P. Cañizares and A. D. Lucas, *Desalination*, **286**, 193 (2012).
30. S. Y. Tang and Y. R. Qiu, *Korean J. Chem. Eng.*, **36**, 1321 (2019).
31. Q. Zhang, J. Gao and Y. R. Qiu, *Chem. Eng. Process.*, **135**, 236 (2019).
32. J. Y. Xu, S. Y. Tang and Y. R. Qiu, *J. Cent. South Univ.*, **26**, 577 (2019).
33. B. Y. Spivakov, V. M. Shkinev, V. I. Golovanov, E. Bayer and K. E. Geckeler, *Theory. Simulations*, **5**, 357 (1996).
34. R. S. Juang and C. H. Chiou, *J. Membr. Sci.*, **177**, 207 (2000).
35. G. Boczkaj and A. Fernandes, *Chem. Eng. J.*, **320**, 608 (2017).
36. Y. R Qiu and L. J. Mao, *Desalination*, **329**, 78 (2013).
37. P. Gull, M. A. Malik, O. A. Dar and A. A. Hashmi, *J. Mol. Struct.*, **1134**, 734 (2017).
38. J. Llanos, R. Camarillo, Á. Pérez and P. Cañizares, *Sep. Purif. Technol.*, **73**, 126 (2010).
39. P. Cañizares, A. Pérez, R. Camarillo and R. Mazarro, *J. Membr. Sci.*, **320**, 520 (2008).
40. S. Y. Tang and Y. R. Qiu, *Korean J. Chem. Eng.*, **35**, 2078 (2018).
41. R. Bouzerar, M. Y. Jaffrin, L. H. Ding and P. Paullier, *Aiche J.*, **46**, 257 (2000).
42. H. Llerena-Chavez and F. Larachi, *Chem. Eng. J.*, **64**, 2113 (2009).
43. X. Z. Jian, Q. Y. Hong, N. D. Huang, J. F. Liu and F. Z. Li, *Chemosphere*, **76**, 706 (2009).