Selective separation of heavy metals from printed circuit board rinse wastewater via shear-induced dissociation coupling with ultrafiltration

Hui-Shang Le, Han Zhou, Yun-Ren Qiu*

*School of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China,
emails: csu_tian@csu.edu.cn (Y.-R. Qiu), 1294292979@qq.com (H.-S. Le), 3059987729@qq.com (H. Zhou)*

ABSTRACT

Removal of M (Cu(II), Ni(II), Pb(II), Zn(II), Ca(II)) from the printed circuit board (PCB) rinse wastewater by complexation–ultrafiltration (C–UF) using a copolymer of maleic acid-acrylic acid (PMA) with a high content of carboxylic groups as a complexing agent was investigated. The effects of pH and P/M (mass ratio of polymer to metal ions) on the simultaneous removal of M via C–UF were studied in detail and the rejections of the above ions can approach 99% at the optimized pH 7.0 and P/M 8. Furthermore, the shear stabilities of PMA-M complexes were studied using rotating disk membrane (RDM), and the sequence of the shear stabilities of the complexes is PMA-Cu > PMA-Ni > PMA-Pb > PMA-Ca > PMA-Zn at pH 7.0. The great differences in shear stabilities of complexes were applied for selective separation of Cu(II), Ni(II), Pb(II), Ca(II) and Zn(II) from PCB plant wastewater as well as the regeneration of PMA by shear-induced dissociation coupling with ultrafiltration (SID-UF). High selective separation coefficients (β) of metals were obtained using SID-UF, and the maximum $\beta_{Zn/Ca}$, $\beta_{Ca/Pb}$, $\beta_{Pb/Ni}$ and $\beta_{Ni/Cu}$ are 103.3, 85.2, 73.8, and 63.6, respectively. Moreover, the regenerated PMA can be directly used as a complexing agent, thus SID-UF exhibits a promising potential for separation of heavy metals from effluent.

Keywords: Heavy metals; Selective separation; Ultrafiltration; Shear stability; Shear-induced dissociation

1. Introduction

The printed circuit board (PCB) rinse wastewater, containing different concentrations of copper, zinc, nickel, lead, tin, iron and aluminum ions, etc., is a serious risk to human health and ecological systems on earth [1–4]. Besides, there are significant economic rewards in extracting heavy metal ions from wastewater due to their unique physical and chemical characteristics [5–8]. Hence, it is essential to develop efficient and economical methods to separate and recycle these contaminants from wastewater before discharge to the environment.

Various chemical and physicochemical methods have been employed for the recovery of heavy metals from PCB plant wastewater. Kao and Liu explored the recovery of heavy metals from PCB plant wastewater via ammonia extraction [9]. Tu et al. [10] performed a method to recover Cu(II) from PCB wastewater by acid leaching coupling with a chemical exchange. Xie et al. [11] showed that ultrasound had the potential for the separation of heavy metals in PCB industry wastewater. Wu et al. [12] investigated the recovery of metals from PCB plant wastewater by microwave-assisted acid extraction. Although the extraction and acid leaching can achieve selective separation of metals, most of the reagents produced by this process are harmful to the environment [13]. Chemical exchange and ultrasound have been considered as promising ways to remove the metal ions in the effluent, but these technologies show complicated

* Corresponding author.

conditions and high operational costs [13,14]. Thus, the practical application of the above-discussed technologies remains a challenge. It calls for the development of efficient and green processes for selective separation of heavy metal ions from PCB plant wastewater.

During recent years, with the advantages of high efficiency and low energy requirement, ultrafiltration-based separation processes combined with complexant, including polyacrylate sodium [15,16], polyethyleneimine [17], chitosan [18] and the copolymer of maleic acid-acrylic acid (PMA) [19], has successfully aroused the interest of many researchers. This process is based on the principle that pH sensitivities of polymer-metal complex formation vary significantly from metal to metal so that heavy metals can be selectively separated by acidification dissociation [20–23]. Some researchers have already been undertaken by means of the process. Zeng et al. [15] studied the selective separation of Hg(II) and Cd(II) from aqueous solutions using polyacrylate sodium as complexing agent [24]. Cañizares et al. [25] investigated the selective recovery of cadmium and lead from aqueous effluents by poly (acrylic acid) as complexant. Selective separation of Cu(II) and Ni(II) from aqueous systems can be achieved by polyethyleneimine [26]. Although this process can achieve the separation of heavy metal ions, not only it consumes a large number of acids and alkali leading to the waste of resources, but also it is difficult to attain high selectivity and efficiency for separation of heavy metal ions from a diverse mix of elements [22,27]. Moreover, a large amount of polymer is present in the wastewater in this process which results in the production of secondary wastes.

The shear stabilities of polymer-metal complexes, such as PAA-Ni [28], PAA-Cr [29], PAA-Cu [30] and PMA-Sn [31], were investigated in our previous study, the results showed that the polymer-metal complex would dissociate when the shear rate exceeded the critical shear rate γ_c (the smallest shear rate at which the polymer-metal complexes begins to dissociate). Herein, a novel technique, called shear-induced dissociation coupling with ultrafiltration (SID-UF), is presented for the separation and recovery of metals from wastewater. SID-UF mainly includes two processes, heavy metals are first bound with a polymer to form polymer-metal complexes which can be rejected by ultrafiltration to remove metals, and then metal ions are separated selectively and polymer is regenerated by shear-induced dissociation coupling with ultrafiltration according to the differences of the shear stabilities of polymer-metal complexes. In comparison to conventional separation methods, the advantages of SID-UF are the high separation efficiency, no secondary pollution and the high recovery efficiency of regenerated complexant [29]. SID-UF has been used to effectively separate Ni(II) and Cr(III) from a simulative solution by accurately controlling the shear rate [29]. However, to date, the treatment for PCB wastewater via SID-UF has not been reported.

The objective of this paper was to investigate the selective separation of M (Cu(II), Ni(II), Pb(II), Zn(II), Ca(II)) from PCB rinse wastewater by SID-UF using PMA as a complexing agent. For this aim, the first work was performed to determine the optimized conditions for the simultaneous rejection of M by ultrafiltration. The second part of this study

was to explore the shear stabilities of PMA-M complexes and calculate the corresponding critical shear rate. Further work was to investigate the effects of shear rate (γ) on selective separation coefficient, so as to lay the foundation for the following SID-UF. Finally, SID-UF was conducted for the selective recovery of metal ions and the regeneration of PMA from PCB industry wastewater.

2. Materials and methods

2.1. Chemicals and membrane

The experimental PCB rinse wastewater was obtained from the wastewater treatment plant of a printed circuit board factory located in Changsha, China. The metal ions composition of wastewater is analyzed by ICP-OES (Optima 8000, Perkin Elmer, USA) and the initial metal ions composition of the real wastewater samples are listed in Table 1. $CuSO_4 \cdot 5H_2O$, $NiSO_4 \cdot 6H_2O$, $Pb(NO_3)_2$, $ZnCl_2$, and $CaCl_2$ provided by Shanghai Chemical Reagent Station (China) were used as M (Cu(II), Ni(II), Pb(II), Zn(II), Ca(II)) sources, for simulated mixed solutions. The pH of the solution was adjusted by adding hydrochloric acid (0.1 M) or sodium hydroxide (0.1 M). All chemicals were of analytical grade. All the solutions in the experiment were prepared with deionized water. A copolymer of maleic acid -acrylic acid (PMA, MW = 70 kDa) was supplied by Shenyang Xingqi Daily Chemicals Plant, China. The structure of PMA is shown in Fig. 1, the high content of the carboxyl group is a significant feature and possibly corresponding to a high capacity of metal ions [19]. Before complexation, the PMA solutions were pre-treated to eliminate smaller molecular fractions [32]. PES flat ultrafiltration membrane with molecular weight cut-off (MWCO) 20 kDa was provided by Shanghai Yuling Filter Equipment Co., Ltd., China.

2.2. Experimental procedures

2.2.1. C–UF Experiment

C–UF and SID-UF experiments are performed in the experimental set-up described in our previous work [31].

Table 1
Concentrations of heavy metal ions in real wastewater samples at different stages

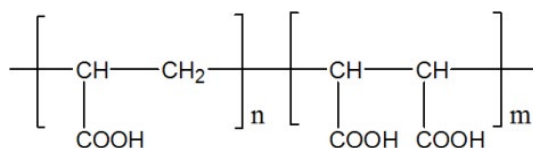| Parameters	Initial composition	After precipitation	After complexation–ultrafiltration
Final pH	2.6 ± 0.5	7.0	7.0
Cu(II) (mg L^{-1})	136.2 ± 0.3	63.7	<0.1
Zn(II) (mg L^{-1})	115.0 ± 0.3	87.3	<0.1
Ni(II) (mg L^{-1})	96.3 ± 0.1	90.5	<0.1
Pb(II) (mg L^{-1})	36.2 ± 0.3	33.2	<0.1
Ca(II) (mg L^{-1})	23.6 ± 0.2	22.9	<0.1
Sn(II) (mg L^{-1})	31.2 ± 0.1	<0.1	–
Al(III) (mg L^{-1})	12.1 ± 0.1	<0.1	–
Fe(III) (mg L^{-1})	32.6 ± 0.5	<0.1	–

Fig. 1. Chemical structure of PMA.

The UF experiment was conducted in a full recycling process with a total volume of 2 L for each experiment. The retentate and permeate were returned to the reservoir to keep the concentration of feed constant. A simulated solution containing M (Cu(II), Ni(II), Pb(II), Zn(II), Ca(II)) or pretreated real wastewater were mixed with the PMA to form PMA-M complexes solution, and the mixed solution was fully stirred for 2 h to ensure that M were all integrated by PMA. The mixture was introduced to the 2 L feed reservoir and circulated through the RDM module. Working pH was adjusted to 7.0 and P/M was increased in steps. The average metal ions concentration of three permeate samples was used to calculate the removal rate for metal ions. The trans-membrane pressure was 10 kPa. All experiments were at 25°C. The concentrations of different metal ions and the concentrations of the PMA solution were measured by ICP-OES (Optima 8000, Perkin Elmer, USA) and total organic carbon (TOC-DCSH, Japan), respectively. The pH value was gauged by a digital display pH meter (PHS-25, China).

2.2.2. SID-UF Experiment

The metals in real wastewater were first bound with PMA to form 4 L PMA-M complexes solution at pH 7.0 and P/M 8 (according to UF experiments), and the obtained solution was filled into the 2 L feed reservoir by a peristaltic pump at feed rate 30 L/h. Then, the selective separation of heavy metals and regeneration of PMA was performed by controlling the proper rotating speed of rotating disk according to the great difference in shear stabilities of PMA-M complexes. An amount of hyper pure water was added to the raw material tank simultaneously to maintain the constant volume of feed. After the concentration of target metal ions remains constant in the retentate, the rotating speed was changed to recover the next metal. In the experiments, the concentration polarization and membrane fouling can be neglected due to the strong shear action on the membrane surface caused by the rotating disk membrane module [30]. The separation efficiency was determined by measuring the concentration of M in the retentate. All tests were repeated at least three times. The errors were controlled below 5%.

3. Results and discussion

3.1. Removal of Sn(II), Al(III) and Fe(III) by chemical precipitate

Initial ICP results on the real wastewater collected from a wastewater treatment plant of a printed circuit board factory indicates that the total metal contents in the wastewater were 136.2 mg/L for Cu(II), 115.0 mg/L for Zn(II), 96.3 mg/L for Ni(II), 36.2 mg/L for Pb(II), 31.2 mg/L for Sn(II), 23.6 mg/L for Ca(II), 12.1 mg/L for Al(III) and 32.6 mg/L for Fe(III) (Table 1). Because the content of Mg(II) was much

lower than other metal ions in the PCB rinse wastewater, the experimental result for Mg(II) was not considered and not discussed in this study. The pH of wastewater was analyzed by a digital display pH meter and the average pH of wastewater is 2.6. These metal ions in wastewater are pretreated by chemical precipitation (adjusting the pH to 7.0). The pH of the solution was adjusted by sodium hydroxide (0.1 M) and the removal rates of metals at different pHs are displayed in Fig. 2. The removal rate of metals (abbreviated as R) is calculated with the following Eq. (1):

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \tag{1}$$

where C_p and C_f are the concentration (mg/L) of metal ions in the permeate and feed, respectively. As can be seen in Fig. 2, the rejections of Cu(II), Zn(II), Ni(II), Pb(II), Ca(II), Sn(II), Al(III) and Fe(III) are 53.2%, 24.1%, 6.0%, 8.3%, and 3.0%, respectively. Chemical precipitation is capable of reducing the concentrations directly from the primary concentration to <0.1 mg/L for Sn(II), <0.1 mg/L for Fe(III) and to <0.1 mg/L for Al(III), while the concentrations of Cu(II), Zn(II), Pb(II), Ni(II) and Ca(II) are 63.7, 87.3, 33.2, 90.5, and 22.9 mg/L, respectively (Table 1). The following experiments were carried out with the use of pre-treated wastewater.

3.2. Simultaneous removal of Cu(II), Zn(II), Pb(II), Ni(II) and Ca(II) in PCB rinse wastewater via C–UF

In order to remove Cu(II), Zn(II), Pb(II), Ni(II) and Ca(II) completely by UF and ensure the effective utilization of PMA, the effect of P/M on the simultaneous removal of heavy metals was examined under neutral condition using the simulated wastewater containing 63.7 mg/L Cu(II), 87.3 mg/L Zn(II), 33.2 mg/L Pb(II), 90.5 mg/L Ni(II) and 22.9 mg/L Ca(II). The neutral condition (pH, 7.0) was used in this work to avoid the formation of metal hydroxides at slightly alkaline pH values and the neutral condition
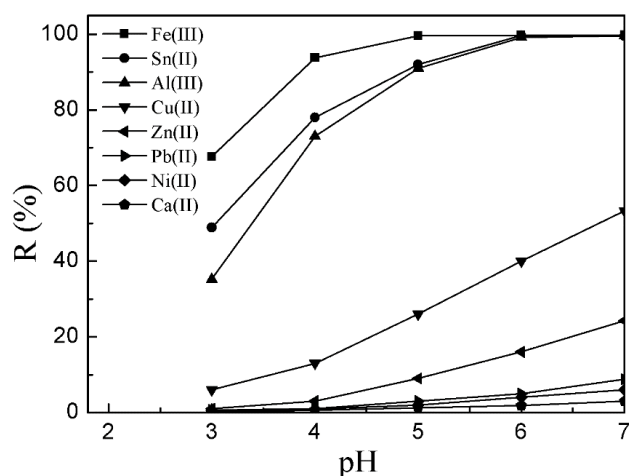

Fig. 2. Effect of pH on the removal rates of metals by chemical precipitation.

is safe for operation and friendly for the environment. The results are illustrated in Fig. 3. It is clearly observed that the P/M has significant effects on the elimination of the metal, and the removal efficiency is increased by P/M rise, which agrees with the previous study. When P/M exceeds 6, the removal rate of copper, zinc, lead, nickel and calcium ions all approach 99%, indicating that free metal ions in the solution are all bound by the PMA. Cañizares et al. [25] suggested that the limited active sites in polymers were preferentially occupied by metal ions with the stronger binding ability. Thus the experimental results show that the sequence with regards to complexing abilities of PMA was Cu(II) > Ni(II) > Pb(II) > Ca(II) > Zn(II).

PCB wastewater was also used to explore the influences of P/M on the removal rate of heavy metals in UF process, and the results are presented in Fig. 3. It can be seen that the metal ions rejections of PCB wastewater are comparatively lower than that of simulated wastewaters under the same P/M. This can be interpreted by the fact that there exists the competition of complexation between background electrolyte (Mg(II), Na(I), K(I)) and target metal ions in the PCB wastewater treatment, resulting in decreasing the binding of PMA and metal ions [33]. Other possible explanation is that NaCl or Na_2SO_4 in the real wastewater probably leads to the compressing electric double layer, which causes a reduction in the electrostatic attraction between charged polymers and metal ions leading to lower retention [18,34,35]. As can be seen in Fig. 3, the rejections of all metal ions approaches 99% when P/M exceeds 8, indicating that free metal ions in the solution are all bound by the complexant. This is because a sufficient amount of PMA can greatly increase the possibility of metal ions complexing with PMA [19]. In addition, the concentrations of metal ions after ultrafiltration have been reduced to less than 0.1 mg/L (Table 1). Considering from the economical cost of PMA and the removal rate of metal ions, P/M 8 and pH 7.0 are chosen as the optimized conditions for simultaneous rejection of Cu(II), Pb(II), Ni(II), Ca(II) and Zn(II) by C–UF.

3.3. Distribution of shear rate on the membrane surface

Bouzerar et al. [36] derived the Eqs. (2) and (3) of shear rate (γ_m) on the membrane surface as follow:

$$\gamma_{ml} = 0.026\upsilon^{-0.5}\left(kN\right)^{1.5} r = 0.77\upsilon^{-0.5}\left(k\omega\right)^{1.5} r \qquad (2)$$

$$\gamma_{mt} = 0.0005\upsilon^{-0.8}\left(kN\right)^{1.8} r^{1.6} = 0.0296\upsilon^{-0.8}\left(k\omega\right)^{1.8} r^{1.6} \qquad (3)$$

Where γ_{ml} and γ_{mt} are the shear rates generated by the rotating disk in laminar ($N \leq 570$ rpm) and turbulent ($N > 570$ rpm) flow, respectively. N is the rotating speed (rpm) of the disk. υ is the kinematic viscosity of the treated fluid ($m^2\ s^{-1}$). ω is the angular velocity of disk. r is the membrane radius. k represents the velocity factor defined as the velocity ratio of the main fluid to the circular disk and it is only related to the device geometry [36,37]. The k value of the rotating disk with six vanes using in this study is 0.796 according to the earlier publication from our laboratory [30]. Fig. 4 shows the distribution of shear rate γ along the membrane
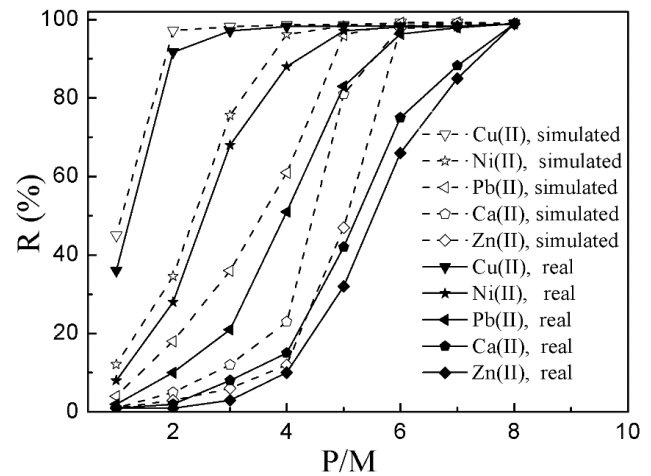

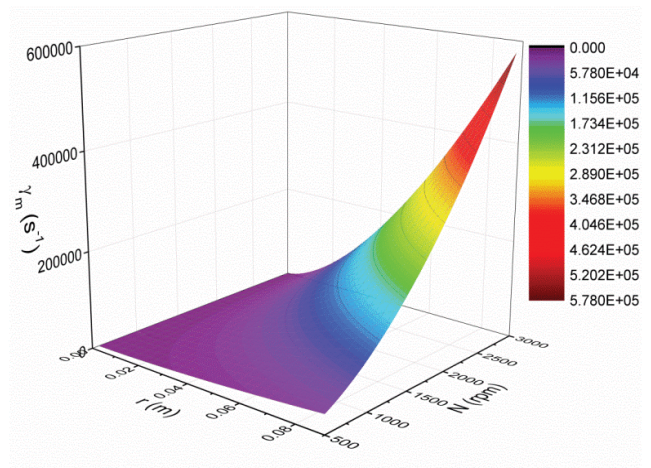Fig. 3. Effect of P/M on the rejections of metal ions at pH 7.0.

Fig. 4. Radial distribution of shear rate on the membrane surface at different rotating speeds.

radius at various rotating speeds N. The γ increases with N, and it increases together with the radius at a given N. This conclusion indicates that the position further from the center of membrane generated larger radial velocity gradient, which agrees with previously published paper [38,39].

3.4. Shear stabilities of PMA-M complexes

The mixture solution of PMA with PCB wastewater was prepared to form feed solutions. According to the results of section 3.2, the pH and P/M of the feed solutions were adjusted to 7.0 and 8, respectively, which can ensure that the heavy metals are bonded completely. The feed solution was introduced to the 2 L feed tank and circulated through the RDM module. The rotating speed was increased in steps. The influence of shear rate on the stabilities of PMA-M complexes was investigated. The variation of the removal rate of metal ions with rotating speed at pH 7.0 was obtained, as it is displayed in Fig. 5. It is worth noting that the rejection rate of metal ions initially remains constant and then the rejection
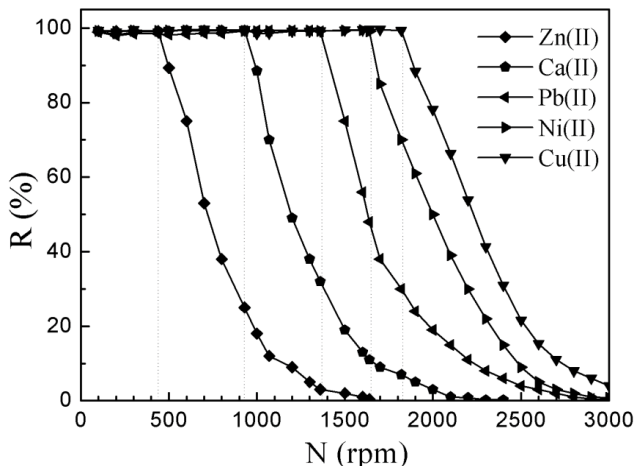
Fig. 5. Effect of rotating speed on the rejection of metal ions in wastewater.

Fig. 6. Distribution of the form of metals on the membrane surface in the shear field (inorganic anions and sodium omitted).

rate will have a sudden drop when N exceeds a certain speed. This could be attributed to the fact that the dissociation of the polymer-metal complex at the high shear rate generated by the RDM, which resulted in the reduction of the metal rejection [29,30]. The critical rotating speed (N_c) is defined as the smallest rotating speed at which the polymer-metal complexes begin to dissociate [30]. As described in Fig. 5, the critical rotating speeds of PMA-Zn, PMA-Ca, PMA-Pb, PMA-Ni and PMA-Cu complexes are 440, 930, 1,360, 1,640 and 1,820 rpm, respectively.

According to the distribution of shear rate on the membrane surface, it is conceivable that the complexes near the center of the membrane will remain stable even if the complexes near the edge of the membrane have dissociated at a certain N. Thus, the segmentation model on the membrane surface was established to reveal the distribution of PMA-M complexes in the shear field, and it is presented in Fig. 6. Where r_i is the membrane inside radius, r_o is the outer radius of the membrane. The critical shear radius (r_c) is defined as the radius where PMA-M begins to dissociate [28]. When $r_c < r < r_o$, PMA-M complexes are completely dissociated, and the M concentration in the permeate (C_{dis}) is equal to the M concentration in feed stream (C_f). When $0 < r < r_c$, the PMA-M complexes can keep stable and can be retained by the membrane, and the M concentration in permeate (C_{com}) is equal to the concentration of permeate in the static filtration (C_0). Tang et al. [30] have obtained the Eq. (4) of r_c by the principle of material balance and segmentation model, the representation is expressed as:

$$r_c^4 + \frac{364P_0}{\rho k^2 N^2} r_c^2 + \frac{C_p - C_f}{C_f - C_0}\left(r_o^4 + \frac{364P_0}{\rho k^2 N^2} r_o^2\right) + \frac{C_0 - C_p}{C_f - C_0}\left(r_i^4 + \frac{364P_0}{\rho k^2 N^2} r_i^2\right) = 0$$

(4)

where P_0 is the pressure at the membrane center and ρ is the density of the solution (kg m^{-3}). C_p is the M concentration in permeate. k represents the velocity following factor. The k value of the rotating disk with six vanes using in this study is 0.796 according to the data taken from an earlier publication from our laboratory [40]. Inserting the experimental data
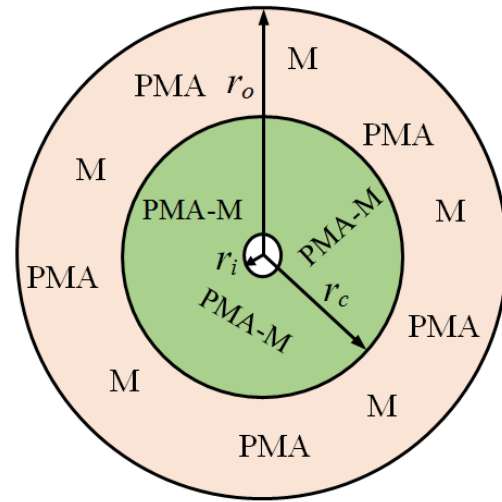
in Fig. 5 into Eq. (3), the relationship between the r_c and the N can be obtained, and the corresponding relation is measured by fitting curves which are shown in Table 2. The r_c significantly decreases with the rising N. This result might be explained as follows: the dissociation region is extended to the membrane center with the N increasing, leading to the r_c decrease [28].

In order to further explain the shear stabilities of the PMA-metal complexes, the γ_c of the PMA-M complexes were calculated according to r_c and Eq. (2) [30,36]. As it is observed in Fig. 7, the γ_c of PMA-Zn, PMA-Ca, PMA-Pb, PMA-Ni, and PMA-Cu complexes are 1.81×10^4, 6.97×10^4, 1.38×10^5, 1.94×10^5, and 2.33×10^5 s^{-1}, respectively. The results indicate that the order of the shear stabilities of the complexes is PMA-Cu > PMA-Ni > PMA-Pb > PMA-Ca > PMA-Zn at the pH 7.0.

3.5. Selective separation of heavy metals and regeneration of PMA by SID-UF

On the basis of Section 3.4, the PMA-M complex will dissociate when the γ is greater than the γ_c of complex, so we can utilize this property to selectively separate heavy metals by SID-UF according to γ_c of PMA-M complexes greatly vary from metal to metal. The shear rate plays a critical role in the removal rate of metal ions by C–UF, thus it is essential to explore optimized shear rate for selective separation of Cu(II), Zn(II), Pb(II), Ni(II) and Ca(II) by SID-UF.

3.5.1. Optimized conditions of selective separation

The selective separation coefficient (β) was used to describe the separation quantitatively [29,41]. β of both metals can be defined as:

$$\beta_{A/B} = \frac{C_{p,A}}{C_{p,B}} \bigg/ \frac{C_{f,A}}{C_{f,B}} = \frac{C_{p,A}}{C_{f,A}} \bigg/ \frac{C_{p,B}}{C_{f,B}} = \frac{1 - R_A}{1 - R_B}$$

(5)

Table 2
Correlations of r_c and N at pH 7.0

Complexes	N_c (rpm)	r_c (m)	Regression coefficient (R^2)
PMA-Zn	440	$r_c = 82\ N^{-1.125}\ (N \geq 440)$	0.997
PMA-Ca	930	$r_c = 191\ N^{-1.125}\ (N \geq 930)$	0.999
PMA-Pb	1,360	$r_c = 294\ N^{-1.125}\ (N \geq 1,360)$	0.998
PMA-Ni	1,640	$r_c = 362\ N^{-1.125}\ (N \geq 1,640)$	0.997
PMA-Cu	1,820	$r_c = 408\ N^{-1.125}\ (N \geq 1,820)$	0.998
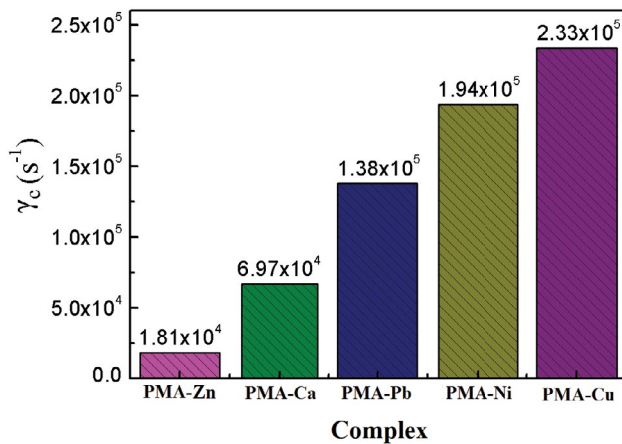
Fig. 7. Critical shear rates of PMA-M complexes at pH 7.0.

Fig. 8. Effect of rotating speeds on selective separation coefficient (β) at pH 7.0.

where R_A and R_B are removal rates of metal A and metal B, respectively. The C_p and C_f are the concentrations of metal ions in the permeate and feed solution, respectively. β is the main criteria for evaluation of the performance of selective separation, and the higher β value ensures the greater separation performance of metals [29].

To explore optimized conditions for the selective separation of metal ions, the effect of the rotating speed on $\beta_{Ca/Zn}$, $\beta_{Ca/Pb}$, $\beta_{Pb/Ni}$ and $\beta_{Ni/Cu}$ were investigated at the rotating speed between 0 and 3,000, and the results obtained are presented in Fig. 8. With the increase of the rotating speed, β represents a tendency of constant first, and then it rises to a maximum value and rapidly decreases subsequently. The phenomenon may be explained as follows: at low N, PMA-M complexes could keep stable, making the rejections of all metal ions high and β low. As N continues increases, when N reaches the N_c of the PMA-M$_A$ complex so that the PMA-M$_A$ complex will dissociate, which results in the R_A decreases and the value of β represents an enlargement tendency. The R_B starts to decrease once the N is beyond N_c of the PMA-M$_B$, resulting in the reduction of β. As shown in Fig. 8, the maximum $\beta_{Zn/Ca}$, $\beta_{Ca/Pb}$, $\beta_{Pb/Ni}$ and $\beta_{Ni/Cu}$ are 103.3, 85.2, 73.8 and 63.6 at 850, 1,270, 1,560 and 1,750 rpm, respectively. And the corresponding shear rates are 5.93×10^4, 1.22×10^5, 1.77×10^5 and 2.17×10^5 s^{-1}, respectively. This experimental results can be further inferred that selective separation of Cu(II), Zn(II), Pb(II), Ni(II) and Ca(II) from PMA-M complexes solution can be achieved by controlling the appropriate rotating speed.
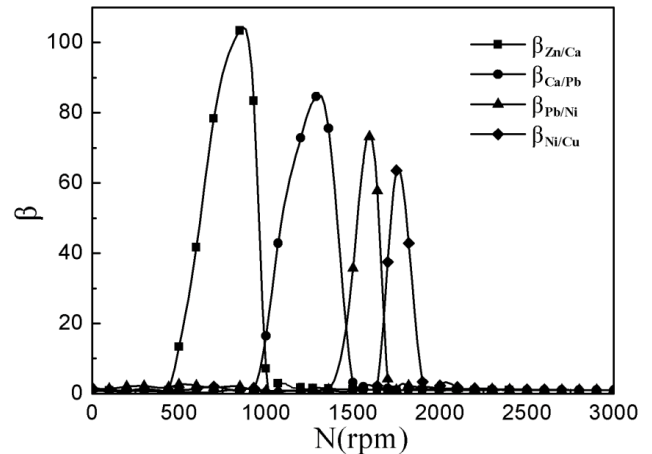
3.5.2. Selective separation of Cu(II), Ni(II), Pb(II), Zn(II) and Ca(II)

After the treatment of metals from PCB rinse wastewater by chemical precipitate, residual metal ions were mixed with PMA to form PMA-M complexes solution at conditions of pH 7.0 and P/M 8. Then, SID-UF experiments were carried out to selective separation of Cu(II), Zn(II), Pb(II), Ni(II) and Ca(II) from complexes solution, and the results are observed in Fig. 9. Where V_R is the volume ratio of make-up deionized water vs. raw material, C_R denotes the concentration ratio of retentate vs. raw material. In the shear field of 850 rpm (5.93×10^4 s^{-1}), the C_R of Zn(II) decreases rapidly with an increase in V_R since that the PMA-Zn complex is easily dissociated. When $V_R \geq 7.0$, Zn(II) can be entirely recovered. And then, the N was raised to 1,270 rpm (1.22×10^5 s^{-1}) for recovery of Ca(II), PMA-Ca will dissociate because the γ is greater than the γ_c of PMA-Ca complex (6.97×10^4 s^{-1}), thus the content of Ca(II) in the retentate decreases obviously. As displayed in Fig. 9, the recovery of Ca(II) is successfully realized at $V_R \geq 10.0$. Similarly, the rotating speed was adjusted to 1,560 rpm (1.77×10^5 s^{-1}) for the separation of Pb(II). When $V_R \geq 14.0$, Pb(II) would completely entered to the permeate. Further, the recovery of Ni(II) can be achieved at 1,750 rpm, and Ni(II)) is recovered completely at $V_R \geq 22.0$.

3.5.3. Regeneration of PMA

Having achieved the selective separation of Cu(II), Ni(II), Pb(II), Zn(II) and Ca(II), SID-UF was performed to regenerate PMA at $N > N_{c(Cu(II))}$ (2,100 rpm, $\gamma = 3.02 \times 10^5$ s^{-1}). As illustrated in Fig. 9, the decreasing C_R of Cu(II) increases with the improvement of V_R, while the C_R of PMA stays constant and approaches 1. When the V_R reached 28.0, the C_R of Cu(II) drops to almost 0. Then the diafiltration experiment was conducted without any water to the feed tank, and the regenerated PMA is got about 15 min later.

Moreover, the complex performance of regenerated PMA was evaluated. The simulated solution of 10 mg/L Zn(II) was used in this experiment. The regenerated PMA
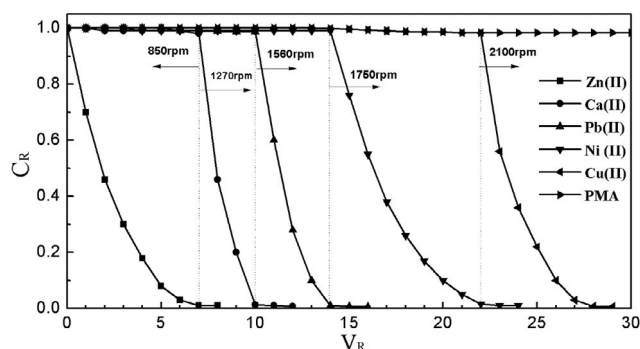
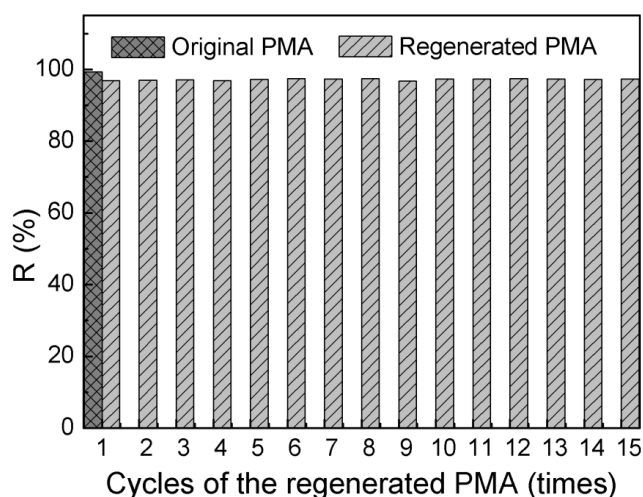Fig. 9. Effect of V_R on C_R of metal ions and PMA (pH 7.0 and P/M 8).

Fig. 10. Variations of the rejection of Zn(II) with different times of the regenerated PMA cycles (pH 7.0 and P/M 25).

and original PMA were used to remove Zn(II) by UF at the optimum conditions [30]. PMA was regenerated for 15 times, and Fig. 10 shows the effect of regeneration times on the removal rate of Zn(II). It is clearly observed from Fig. 10, although the PMA has been regenerated 15 times, the removal rate of Zn(II) can still reach ~ 98% using regenerated PMA. It can be seen that the complexing ability of regenerated PMA is excellent. In addition, the Zn(II) rejection of using regenerated PMA is slightly lower than that of using original PMA, which can be explained by the fact that there still remained very few undissociated PMA-M in regenerated PMA solution, it causes that active sites in regenerated PMA are comparatively lower than in original PMA under same P/M [30]. All these results suggest that SID-UF can be efficiently used for the recovery of metals from PCB plant wastewater and the regeneration of PMA.

4. Conclusions

In summary, we have developed a novel method to remove and selectively separate heavy metal ions from PCB plant wastewater using PMA as complexant via SID-UF according to the great differences in shear stabilities of PMA-M complexes. The effects of pH and P/M on the simultaneous removal of Cu(II), Ni(II), Pb(II), Zn(II) and Ca(II) in C–UF process were investigated and the rejections of the above ions can approach 99% at the optimized pH 7.0 and P/M 8. The shear stabilities of PMA-M complexes were investigated and the results indicate that the order of the shear stabilities of the complexes is PMA-Cu > PMA-Ni > PMA-Pb > PMA-Ca > PMA-Zn under pH 7.0. The corresponding critical shear rates (γ_c) were calculated as 2.33×10^5, 1.94×10^5, 1.38×10^5, 6.97×10^4 and $1.81 \times 10^4\,s^{-1}$, respectively. In addition, the influences of shear rates on selective separation coefficients were studied. The results show that the maximum $\beta_{Zn/Ca}$, $\beta_{Ca/Pb}$, $\beta_{Pb/Ni}$ and $\beta_{Ni/Cu}$ are 103.3, 85.2, 73.8 and 63.6 at 5.93×10^4, 1.22×10^5, 1.77×10^5 and $2.17 \times 10^5\,s^{-1}$, respectively. The selective separation of metal ions from wastewater and the regeneration of PMA were fulfilled by SID-UF under the optimized shear rates using the rotating disk membrane (RDM). Compared with the traditional separation methods, there are several advantages of SID-UF such as high separation selectivity, simple conditions requirement, no secondary pollution. Thus SID-UF can potentially compliment the current technologies for heavy metals removal and recovery.

References

[1] G. Gwak, D.I. Kim, S. Hong, New industrial application of forward osmosis (FO): precious metal recovery from printed circuit board (PCB) plant wastewater, J. Membr. Sci., 552 (2018) 234–242.
[2] Y.C. Kuan, I.H. Lee, J.M. Chern, Heavy metal extraction from PCB wastewater treatment sludge by sulfuric acid, J. Hazard. Mater., 177 (2010) 881–886.
[3] X. Fengchun, L. Haiying, M. Yang, L. Chuncheng, C. Tingting, H. Zhiyuan, Y. Gaoqing, The ultrasonically assisted metals recovery treatment of printed circuit board waste sludge by leaching separation, J. Hazard. Mater., 170 (2009) 430–435.
[4] P.K. Choubey, R. Panda, M.K. Jha, J.C. Lee, D.D. Pathak, Recovery of copper and recycling of acid from the leach liquor of discarded printed circuit boards (PCBs), Sep. Purif. Technol., 156 (2015) 269–275.
[5] P. Liu, T. Yan, J. Zhang, L. Shi, D. Zhang, P. Liu, T. Yan, J. Zhang, L. Shi, D. Zhang, Separation and recovery of heavy metal ions and salt ions from wastewater by 3D graphene-based asymmetric electrodes: via capacitive deionization, J. Mater. Chem. A, 5 (2017) 14748–14757.
[6] T.J. Afolabi, A.O. Alade, M.O. Jimoh, I.O. Fashola, Heavy metal ions adsorption from dairy industrial wastewater using activated carbon from milk bush kernel shell, Desal. Water Treat., 57 (2015) 1–13.
[7] A. Imyim, C. Thanacharuphamorn, A. Saithongdee, F. Unob, V. Ruangpornvisuti, Simultaneous removal of Ag(I), Cd(II), Cr(III), Ni(II), Pb(II), and Zn(II) from wastewater using humic acid-coated aminopropyl silica gel, Desal. Water Treat., (2015) 1–10.
[8] H.Y. Yen, P.L. Chen, Adsorption of Cd(II) from wastewater using spent coffee grounds by Taguchi optimization, Desal. Water Treat., 57 (2015) 1–8.
[9] J.C. Liu, T.H. Kao, Extraction of Cu and Pb from printed circuit board sludge using ammonia solutions, Water Sci. Technol., 47 (2003) 167–172.

[10] Y.J. Tu, C.K. Chang, C.F. You, J.C. Lou, Recycling of Cu powder from industrial sludge by combined acid leaching, chemical exchange, and ferrite process, J. Hazard. Mater., 181 (2010) 981–985.

[11] F. Xie, T. Cai, M. Yang, H. Li, C. Li, Z. Huang, G. Yuan, Recovery of Cu and Fe from printed circuit board waste sludge by ultrasound: evaluation of an industrial application, J. Cleaner Prod., 17 (2009) 1494–1498.

[12] C.H. Wu, C.Y. Kuo, S.L. Lo, Recovery of heavy metals from industrial sludge using various acid extraction approaches, Water Sci. Technol., 59 (2009) 289–293.

[13] S.Y. Chen, Q.Y. Huang, Heavy metals recovery from printed circuit board industry wastewater sludge by thermophilic bioleaching process, J. Chem. Technol. Biotechnol., 89 (2013) 158–164.

[14] S. Babel, D.D.M. Dacera, Heavy metal removal from contaminated sludge for land application: a review, Waste Manage., 26 (2006) 988–1004.

[15] J.X. Zeng, H.Q. Ye, Z.Y. Hu, Application of the hybrid complexation-ultrafiltration process for metal ion removal from aqueous solutions, J. Hazard. Mater., 161 (2009) 1491–1498.

[16] G. Borbély, E. Nagy, Removal of zinc and nickel ions by complexation-membrane filtration process from industrial wastewater, Desalination, 240 (2009) 218–226.

[17] Y. Huang, D. Wu, X. Wang, H. Wei, D. Lawless, X. Feng, Removal of heavy metals from water using polyvinylamine by polymer-enhanced ultrafiltration and flocculation, Sep. Purif. Technol., 158 (2016) 124–136.

[18] R.S. Juang, C.H. Chiou, Ultrafiltration rejection of dissolved ions using various weakly basic water-soluble polymers, J. Membr. Sci., 177 (2000) 207–214.

[19] Y.R. Qiu, L.J. Mao, Removal of heavy metal ions from aqueous solution by ultrafiltration assisted with copolymer of maleic acid and acrylic acid, Desalination, 329 (2013) 78–85.

[20] R. Camarillo, Á. Pérez, P. Cañizares, A.D. Lucas, Removal of heavy metal ions by polymer enhanced ultrafiltration: batch process modeling and thermodynamics of complexation reactions, Desalination, 286 (2012) 193–199.

[21] M.A. Barakat, E. Schmidt, Polymer-enhanced ultrafiltration process for heavy metals removal from industrial wastewater, Desalination, 256 (2010) 90–93.

[22] J. Müslehiddinoğlu, Y. Uludağ, H.Ö. Özbelge, L. Yilmaz, Effect of operating parameters on selective separation of heavy metals from binary mixtures via polymer enhanced ultrafiltration, J. Membr. Sci., 140 (1998) 251–266.

[23] R. Molinari, P. Argurio, Arsenic removal from water by coupling photocatalysis and complexation-ultrafiltration processes: a preliminary study, Water Res., 109 (2017) 327–336.

[24] X.Z. Jian, Q.Y. Hong, N.D. Huang, J.F. Liu, F.Z. Li, Selective separation of Hg(II) and Cd(II) from aqueous solutions by complexation–ultrafiltration process, Chemosphere, 76 (2009) 706–710.

[25] P. Cañizares, A. Pérez, R. Camarillo, R. Mazarro, Simultaneous recovery of cadmium and lead from aqueous effluents by a semi-continuous laboratory-scale polymer enhanced ultrafiltration process, J. Membr. Sci., 320 (2008) 520–527.

[26] R. Molinari, P. Argurio, T. Poerio, G. Gullone, Selective separation of copper(II) and nickel(II) from aqueous systems by polymer assisted ultrafiltration, Desalination, 200 (2006) 728–730.

[27] J. Llanos, R. Camarillo, Á. Pérez, P. Cañizares, Polymer supported ultrafiltration as a technique for selective heavy metal separation and complex formation constants prediction, Sep. Purif. Technol., 73 (2010) 126–134.

[28] J. Gao, Y. Qiu, M. Li, H. Le, Separation of valuable metals in spent LiNi0.46Co0.2Mn0.34O2 battery by shear-induced dissociation coupling with ultrafiltration, Hydrometallurgy, 189 (2019) 1–7.

[29] Q. Zhang, J. Gao, Y. Qiu, Removal of Ni(II) and Cr(III) by complexation-ultrafiltration using rotating disk membrane and the selective separation by shear-induced dissociation, Chem. Eng. Process., 135 (2019) 236–244.

[30] S. Tang, Y. Qiu, Removal of copper(II) ions from aqueous solutions by complexation–ultrafiltration using rotating disk membrane and the shear stability of PAA-Cu complex, Chem. Eng. Res. Des., 136 (2018) 712–720.

[31] H. Le, Y.Qiu. S. Tang. Qiu, Removal of Sn^{2+} using copolymer of maleic acid-acrylic acid (PMA) by complexation–ultrafiltration and regeneration of PMA using shear-induced dissociation and ultrafiltration, Desal. Water Treat., 160 (2019) 41–49.

[32] J. Xu, S. Tang, Y. Qiu, Pretreatment of poly (acrylic acid) sodium by continuous diafiltration and time revolution of filtration potential, J. Cent. South Univ., 26 (2019) 577–586.

[33] C. Ming, K. Shafer-Peltier, S. Randtke, E. Peltier, Competitive association of cations with poly(sodium 4-styrenesulfonate) (PSS) and heavy metal removal from water by PSS-assisted ultrafiltration, Chem. Eng. J., 344 (2018) 155–164.

[34] S.I. Kadioglu, L. Yilmaz, N. Aydogan, H.O. Ozbelge, Removal of heavy metals from multicomponent metal mixtures by polymer enhanced ultrafiltration: effects of pH, ionic strength, and conformational changes in polymer structure, Sep. Sci. Technol., 45 (2010) 1363–1373.

[35] J. Shao, Q. Shu, J. Davidson, W. Li, Y. He, H.S. Zhou, Recovery of nickel from aqueous solutions by complexation-ultrafiltration process with sodium polyacrylate and polyethylenimine, J. Hazard. Mater., 244–245 (2013) 472–477.

[36] R. Bouzerar, M.Y. Jaffrin, L.H. Ding, P. Paullier, Influence of geometry and angular velocity on performance of a rotating disk filter, AIChE J., 46 (2000) 257–265.

[37] H. Llerena-Chavez, F. Larachi, Analysis of flow in rotating packed beds via CFD simulations—dry pressure drop and gas flow maldistribution, Chem. Eng. Sci., 64 (2009) 2113–2126.

[38] M.Y. Jaffrin, Dynamic shear-enhanced membrane filtration: a review of rotating disks, rotating membranes and vibrating systems, J. Membr. Sci., 324 (2008) 7–25.

[39] K.J. Hwang, S.E. Wu, Disk structure on the performance of a rotating-disk dynamic filter: a case study on microalgae microfiltration, Chem. Eng. Res. Des., 94 (2015) 44–51.

[40] S. Tang, Y. Qiu, Removal of Zn(II) by complexation–ultra-filtration using rotating disk membrane and the shear stability of PAA-Zn complex, Korean J. Chem. Eng., 35 (2018) 2078–2085.

[41] F. Ellouze, B. Seantier, N.B. Amar, A. Deratani, Selective separation of α- and β-cyclodextrins by complexation/ultra-filtration using supramolecular host-guest interaction, Sep. Purif. Technol., 204 (2018) 226–233.