EFFECT OF POROUS POLYSULFONE MEMBRANES'S THICKNESS ON FLUX OF FERUM IONS

Nabilla Bt Mohamed Zaimy, Dr Norin Zamiah Bt Kassim Shaari, and Nurul Aida Bt Sulaiman

Faculty of Chemical Engineering, Universiti Teknologi Mara

Abstract— **Membrane separation has been widely used in removal of heavy metal from wastewater. In this research, the wastewater from electroplating industry that contains high concentration of ferum ion was treated by using integrated complexation method through a thin film composite membrane. Chemical precipitation, ion exchange and adsorption are the example of conventional treatment that have significant disadvantages which are incomplete removal, need high energy and result in toxic sludge [16]. Thus, two types of composite membrane were developed from polysulfone as support layer with polymer blend of PVA/chitosan and hybrid membrane which varied by difference thickness under constant pH value at 7, temperature and pressure at 12 bar. The thickness of polysulfone was varied at 60 μm and 90 μm. The concentration was found below than acceptable range and it shows that composite membrane with hybrid membrane as thin layer has the best performance in percentage removal of ferum ion.**

Keywords- **chitosan; composite membrane; ferum ion; percentage removal; thickness**

1. INTRODUCTION

Hybrid membrane has good mechanical and thermal properties as compared to membrane from pure polymer [2] and it is actually combination of at least two different polymer materials [12]. Method of phase inversion has been practiced in this study to form a polysulfone in solid phase. It is a process which the liquid or soluble state will change into solid state [9]. In this case, the polysulfone in crystal form was supply under high temperature until it melted. The high viscosity of polysulfone will eventually turn into solid after being soaked in water which the formation of solid is actually polysulfone membrane.

While Chitosan acts as biopolymer which composed of abundant natural polymer that is chitin [4]. Chitosan has been claimed as unique because it is also has a properties as chelating agent to form metal complexes [5, 11]. The properties of chitosan that consist of hydroxyl and amino groups help to absorb various organic compound effectively [1]. However, chitosan also have the weakness of poor mechanical stability and biodegradability [2].

The used of thin film composite membrane which represent the integrated complexation method could overcome limitation of polymer which could enhanced ultrafiltration process. The integrated complexation method was introduced which to remove heavy metal effectively. This method produced thin film composite that consists of hybrid membrane and polymer blend of PVA/Chitosan as the barrier layer. The purposes of coating thin layer with polymer blend or hybrid membrane on is to respectively improve the selectivity permeability to water, increase the performance of ferum ions removal and also to improve the mechanical strength of membrane.

From the finding and result obtained in this study, composite membrane with polymer blend of PVA/chitosan as thin layer showed less performance in percentage removal of ferum ion compared to composite membrane with hybrid membrane as thin layer.

Wastewater from electroplating industry in Shah Alam has been used due to high content of ferum ions. The characterization of wastewater and preparation of membrane were conducted before undergo the observation of percentage removal by using atomic adsorption spectrometer (AAS). Wastewater was characterized by determining the Biochemical Oxygen Demand (BOD), Chemical oxygen demand (COD), turbidity, total suspended solids (TSS), pH and concentration of ferum ions. The thickness of polysulfone varied at 60μm and 90μm.

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2. METHODOLOGY

A. Materials

For the characterization of wastewater, the equipment of BOD test system, COD reactor, turbidity meter, TSS spectrometer model 2800, pH meter and AAS were used. For the composite membrane, a membrane solutions from polymer blend PVA/Chitosan and hybrid membrane were prepared.

B. Methods

1) Characterization of wastewater

- Preparation of BOD

The Sample of wastewater consist high content ferum ions were obtained from electroplating industry. Sample of wastewater which labelled as Fe (1) and Fe (2) were obtained from equalization tank and settling tank respectively. The sample were kept in cold room and preserve with small amount of acetic acid. Four litre of distilled water was filled inside 20000 ml beaker. 2 ml of Fe$Cl_3 6H_2$O, C_aCl_2 and phosphate buffer solution were poured. The beaker was leave for two hours with supplied of oxygen from dilution water. Eight flasks which two flasks labelled as Fe (1) and another two flask labelled as Fe (2) have been prepared. 50ml of sample has filled inside each flask and dilution water was poured until full for each flasks. The initial result has been recorded and final result was recorded after five days.

- Preparation of COD

Four sample of Fe (1), Fe (2), dilution of Fe (2) and blank sample were prepared and 2ml of deionized water has filled inside 50ml beaker. The blank sample, Fe (1), Fe (2) filled with deionized water.

Fe (1) was diluted with 250ml dilution factor while Fe (2) with dilution factor 100ml because the colour produce from ferum ions will affect the actual reading. The test tube were place in COD reactor under 150℃ for 2 hours and the samples have been cooled down until 120℃. The sample were taken out from COD reactor and cooled down until reach at room temperature. Shaken the test tube and data was recorded.

Turbidity has been determined by using turbidity meter. The samples were placed inside the meter. Total suspended solid content was obtained by using TSS Spectrometer 2800 while pH of ferum ions was determined by using pH meter. The concentration of ferum ions was tested by using Atomic Absorption Spectrometer (AAS)

2) Preparation of a Polysulfone support membrane.

Phase inversion was used to prepare (PSF) support membrane. 13 g of polysulfone bead was dissolved in 87 g of N-methyl-2-pyrollidone (NMP) in order to produce polysulfone polymer solution with 13wt% of polymer concentration. The mixture was stirred continuously for approximately 4 – 6 hours at 60℃ to get the homogenous solution. The solution was left for several hours at room temperature to avoid from the air bubbles. The polysulfone membrane has been cast by using applicator on a glass plate and the thickness was adjusted at $60\mu m$ and $90\mu m$. The film was immediately immersed in water as coagulation medium for one hour. Then, it was left for 24 hours and placed in an oven for another one hour.

3) Preparation of Thin Film Composites

Two types of membrane which thin film composite consists of hybrid membrane and polymer blend of PVA/Chitosan respectively as thin layer were prepared. The solution of hybrid membrane and polymer blend of PVA/Chitosan was coated on polysulfone support membrane by using a glass rod. The membrane was left for 24 hours at room temperature and subsequently place in oven for one hour at 45 ℃ [6, 7]

3. RESULTS AND DISCUSSION

3.1 Characterization of industrial wastewater

Table 1 shows result of characterization of Ferum Industrial Wastewater

Parameter	Ferum I solution	Diluted Ferum I solution with dilution factor of 250	Ferum II solution	Diluted Ferum II solution with dilution factor of 100
Turbidity	16.4 NTU	160 NTU	2.27 NTU	0.74 NTU
COD	1384.33 mg/L	666.67 mg/L	3922.67 mg/L	28933.33 mg/L
pH	1.95	-	12.37	-
BOD	0.55 mg/L	-	8.23 mg/L	-
TSS	11.67 mg/L	-	1.67 mg/L	-
Ferum ion concentration	2.8191 mg/L	-	0.0918 mg/L	-

Parameter	Value
Turbidity	50 NTU
COD	200 mg/L
pH	5.5 – 9.0
BOD	40 mg/L
TSS	100 mg/L
Ferum ion concentration	5.0 mg/L

Table 2 shows the acceptable condition for the discharged of industrial mixed effluent, Standard B [13].

Table 1 shows the results of Ferum (1) solution which was taken from equalization tank while Ferum (2) was taken from the settling tank from wastewater treatment. By comparing those results with allowable conditions in Table 2, turbidity, pH, BOD, TSS and Ferum concentration were under acceptable conditions. However, the results of COD for Ferum (2) ions show that they are out of acceptable range reading. Thus, the pretreatment needed to be done before discharge the solution to the groundwater. The Fe (1) was used as a sample for testing of performance on composite membrane.

3.2 Performance Testing On Composite membrane

This experiment has used two types of composite membranes which are, i) A polymer blend of PVA and chitosan as thin layer and ii) Hybrid membrane as thin layer at thickness $60\mu m$ and 90 μm. The experiments were conducted for three hours which filtered samples were collected every one hour.

Flux performance is the rate of solute or particle transport in the feed side from the bulk solution toward the membrane. The flow was driven by the pressure across the membrane which it transport the solutes on top of membrane surface. If the membrane is partially, or completely, retentive to a given solute, it will eventually cause the retained solute to accumulate at the upstream surface of the membrane. This phenomenon is generally called as concentration polarization [14]. Flux can be calculated by using the formula as follows :

$$J = \frac{V}{A.t} \tag{1}$$

where
J is the flux rate (mL/cm^2.min)
V is the volume of the filtered sample (mL)
A is the membrane surface area (cm^2)
t is the time taken to collect each sample (min).

In addition, the removal percentage performance is referred to the amount of heavy metal ions being removed by using the composite membrane from initial solution. This removal will indicate and determine the performance of the membrane that filtered the Ferum ions contained in the water sample. The removal percentage performance was calculated as follows :

$$\%\ \text{Removal} = \frac{\text{Initial Ferum (1) concentration} - \text{Final Ferum (1) concentration}}{\text{Initial Ferum (1) concentration}} \times 100\% \tag{2}$$

The results below shows performance of composite membranes with, i) A polymer blend of PVA and chitosan as thin layer (composite A) and ii) Hybrid membrane as thin layer (composite B) on the removals of Ferum ions in three hours.

3.3 Flux performance of Ferum ions

The performance of flux composite A and B with thickness 60 µm show the flux performance higher than composite A and B with thickness 90 µm against time. From figure (b) and (c), the flux obtained show a decreasing reading from first hour until next third hours. Figure (a) shows volume of composite A with the thickness 60 µm decrease linearly every one hour. Hence, this result has been proven when the volume decrease, the permeation of flux also decrease. However, volume of composite B with thickness 60 µm and 90µm were increase linearly until 3^{rd} hour. This is due to the concentration polarization where the retained solute at the top surface was accumulated and the water can no longer pass through it.

From figure (d), the performance flux of both composite with thickness 90 µm have been proven as the volume increase, the flux permeate against time will decrease. This is due to the strength of membrane higher than thickness of 60 µm which allow the liquid passed through the surface with higher retention time. From figure (d), the highest performance of flux was composite A with thickness 60 µm, followed by composite B with thickness of 60 µm, composite A with thickness 90 µm and lastly composite B with thickness 90 µm.

Table 3: Volume of the filtered sample in three hours

Composite Membrane	**Thickness**	**Volume (mL)**		
		1st hour	**2nd hour**	**3rd hour**
Membrane	**60µm**	17.5	16.30	15.40
A	**90µm**	8.40	9.50	10.60
Membrane	**60µm**	16.0	18.0	18.50
B	**90µm**	8.60	9.10	10.20

Table 4: Flux Performance of composite membranes in three hours

C	**Thickness**	**Flux Performance, J (mL/cm^2.min)**		
		1st hour	**2nd hour**	**3rd hour**
Membrane	**60µm**	0.01681	0.00783	0.00493
A	**90µm**	0.00807	0.00456	0.00339
Membrane	**60µm**	0.01537	0.00865	0.00592
B	**90µm**	0.00826	0.00437	0.00327

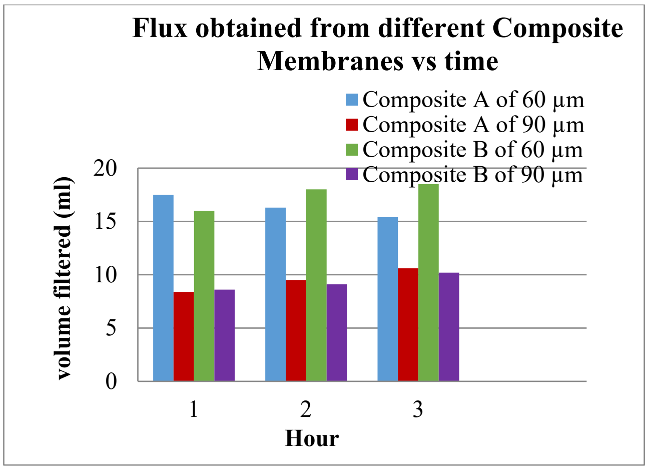

Figure (a): Amount of volume filtered by using composite A and Membrane B in three hours.

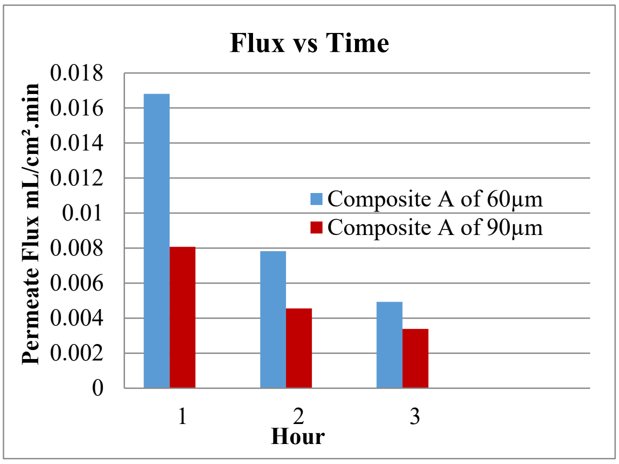

Figure (b): Flux Performance of composite A in three hours

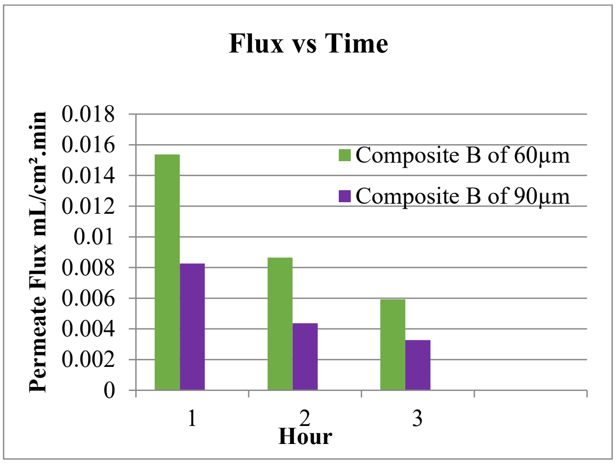

Figure (c): Flux Performance of composite B in three hours

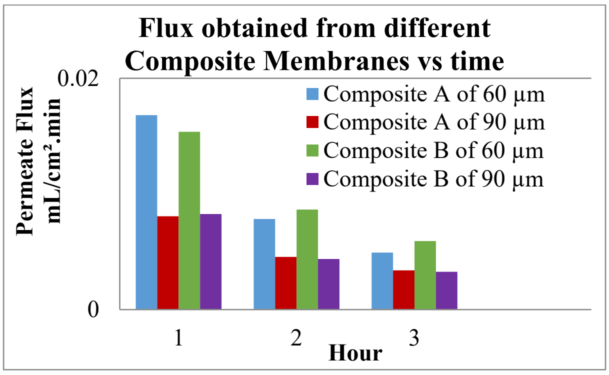

Figure (d): The removal percentage of composite A and composite B of 60 µm in three hours for Ferum (II) ion.

3.4 Removal percentage of Composite membrane

3.4.1 Removal percentage of Ferum (II) ions

From Figure (e), it shows that the removal percentage of composite B of 60 µm is higher than composite A of 60 µm, same goes to Figure (f) that shows the removal of composite B of 90 µm is higher than composite A of 90 µm. Figure (g) shows that the removal percentage of composite B are higher than composite A. The results indicate that performance of both composite from composite B is better than composite A. This is because, composite B was coated with a cross linker TEOS which able to form a compact and less porous structure to the composite which assists the composite to trap more heavy metal ions compared to composite A which was not coated with TEOS. The removal percentage for composite A of 90 µm and composite B of 90 µm are maintained across the three hours with above than 95% percentage removal. This is because the membrane surface was concentrated with retained solute which accumulated at the top surface. Thus, it can no longer pass through the membrane. Composite A at 60 μm has lowest percentage removal (77.94%, 83.77%, 93.68%). This is due to less thickness which the membrane could not withstand the high pressure.

On the other hand, for composite B of 90 µm, it shows the highest removal percentage of Ferum (II) ion with the maximum percentage of 99.22%. It is therefore concluded that composite B at 90 µm is the best membrane showing the highest removal percentage of Ferum (II) ions followed by composite A of 90 µm, composite B of 60 µm and composite A of 60 µm.

Table 5: Removal percentage of the composite membranes in three hours

Composite Membrane	**Thickness**	**Removal percentage (%)**		
		1st hour	**2nd hour**	**3rd hour**
Composite A	**60µm**	77.94	83.77	93.68
	90µm	95.21	95.71	95.77
Composite B	**60µm**	94.50	95.50	95.60
	90µm	98.60	99.15	99.22

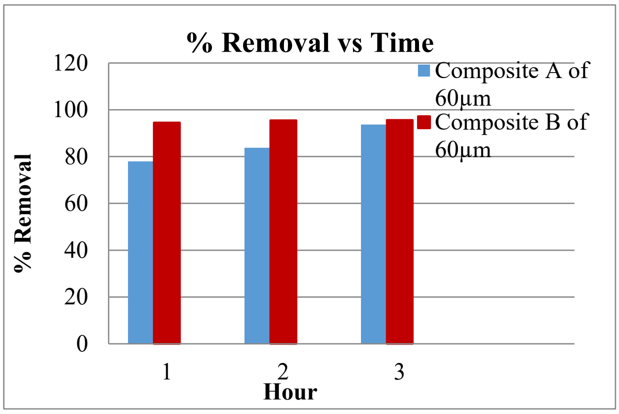

Figure (e): The removal percentage of composite A and composite B of 60 µm in three hours for Ferum (II) ion.

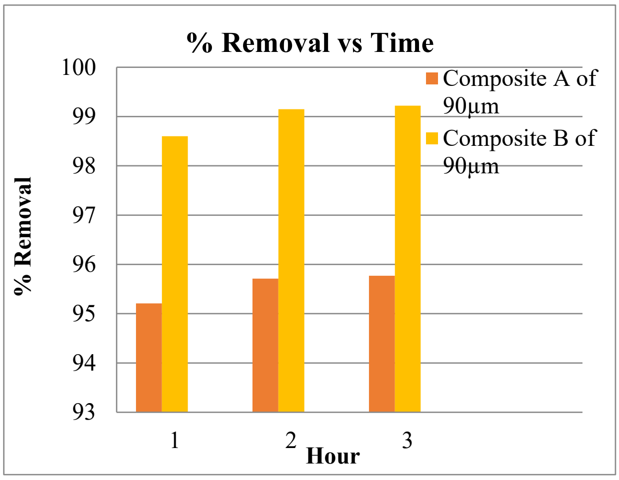

Figure (f): The removal percentage of composite A and composite B in three hours for Ferum (II) ion at 90 μm.

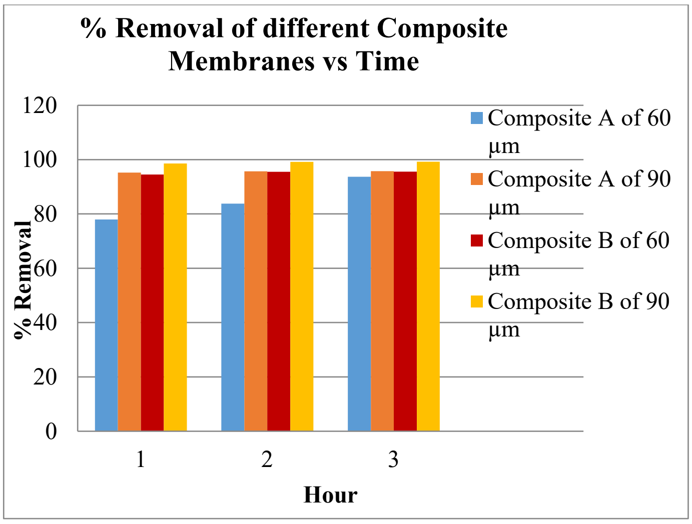

Figure (g) shows the removal percentage of different Composite Membranes in three hours for Ferum (II) ion.

3.5. Concentration of Ferum ions before and after filtration in three hours

From Table 6 and 7, it shows the initial and final concentration Ferum ions in the industrial wastewater before and after the membrane filtration. Based on the Environmental Act 1974, under Environmental Quality (Industrial Effluent) Regulations 2009 of Appendix K2 the concentration of Ferum ions that is allowed to be discharged to groundwater is 5.0 ppm. Therefore, based on Table 7, after the three hours of filtration, only composite B of 90 µm has fulfilled the act's requirements. The final concentration of Ferum ions after three hours filtration for composite B of 90 µm is 1.884 ppm which is below the allowable condition. Therefore, it is concluded that composite B of 90 µm is the best membrane to be used to filter the industrial wastewater sample and the wastewater filtered since this composite membrane can be discharged directly to the groundwater.

Table 6: Concentration of Ferum (II) ions before membrane filtration

Composite Membrane	**Thickness**	**Initial Ferum (II) ions Concentration (ppm)**
Composite A	**60µm**	312.59
	90µm	250.85
Composite B	**60µm**	241.29
	90µm	242.32

Table 7: Concentration of Ferum (II) ions after membrane filtration

Composite Membrane	**Thickness**	**Final Ferum (II) ions Concentration (ppm)**		
		1st hour	**2nd hour**	**3rd hour**
composite A	**60µm**	68.955	50.725	19.765
	90µm	12.000	10.750	10.610
composite B	**60µm**	13.245	10.750	10.610
	90µm	2.518	2.065	1.884

4. CONCLUSION

The result from characterization of industrial wastewater showed that the water sample need to undergo preliminary treatment since the result of COD was out of the acceptable range for the discharged of industrial mixed effluent, Standard B [13]. The results from composite membrane testing by using membrane B have been proven that wastewater from industry electroplating can be discharged to ground water since the concentration of ferum ions very low after being filtered. It was below than acceptable range which is 1.884 ppm. Thus, it has fulfilled the Environmental Act's requirement for effluent discharge.

Results obtained from the finding proves that thickness of membrane will affect the effectiveness of performance in removal of ferum ions. The use of different type of composite membranes also show the significant affect which can determined the mechanical strength of the membranes. The hybrid membrane as the barrier layer showed that the removal of ferum ion can be achieved up to 90% percentage removal.

REFERENCES

[1] Chen Fei, Luo Guangsheng, Yang Weiwei, Wang Yujun, Preparation and Adsorption Ability of Polysulfone Microcapsules Containing Modified Chitosan Gel, 2005, 1-7

[2] L.Y Ye, Q.L Liu, Q.G. Zhang, A.M Zhu, and G.B. Zhou, "Pervaporation characteristics and structure of Polyvinyl alcohol Polyethylene glycol Tetraethoxysilane hybrid membranes," Journal of Applied polymer Science , vol. 105, p. 3640-3648, 2007

[3] Zheng H, Du Y M, Yu J H, Xiao L. The properties and preparation of cross linked chitosan films. Chemical Journal of Chinese University, 2000, 21: 809-812

[4] Muzzarelli r a a, ed Natural Chelating Polymers. New York: Pergamon Press, 1973: 83

[5] Majeti N V, Kumar R.A review of chitin and chitosan applications. Reactive & Functional Polymers, 2000, 46: 1-27

[6] Norin Zamiah, N, A Rahman, and U.T. Mara, Thin film composite membrane with hybrid membrid membrane as the barrier layer: Preparation and characterization, IEE Colloq. Humanit. Sci. Eng. Res (Chuser 2012), pp. 615-620, 2012

[7] N. A. Sulaiman, norin zamiah Kassim Shaari, Norazah Abdul Rahman, "Removal of Cu (II) and Fe (II) ions Trough Thin Film Composite (TFC) with Hybrid Membrane, " J. Eng. Sci Technol ,. No. Special issue on SOMCHE 2015, pp. 36-49, 2016

[8] P. Sossundaran and D. R. Nagaraj, Chemistry and applications of chelating agents in flotation and flocculation pp. 1-11

[9] M. Mulder, Phase Inversion membrane pp. 3331-3332, 2000

[10] Chemical properties of ion (Environment and Health effect of iron, http://www.lenntech.com/periodic/elements/fe.hm

[11] Amass Wendy, Allan Amass and Brian Tighe, Polymer International, pp. 89-144 volume 47, Issue 2, 1998

[12] U. G. K. Wegst and M. F. Ashby, The mechanical efficiency of natural materials, pp 2167-2186, 2007

[13] Environmental Quality (Industrial Effluent) Regulations 2009, Arrangement of Regulations pp. 4010-4059

[14] Aimar,P., Meireles, M., Bacchin, P. and Sanchez, V. 1993. Fouling and Concentration Polarization in Ultrafiltration and Microfiltration. Paper presented at The ASI NATO Meeting , Curia, Portugal March 93

[15] I G. Wenten, Ultrafiltration In Water Treatment and its evaluation as Pre-Treatment For Reverse Osmosis System,pp 1-17

[16] Ho Linlin, Ouyang Tong,Lin Guanghui, Lai Limin, Zhang Jiaoling, Zhang Ping, Removal of Heavy metals from plating wastewater by using complexation-ultrafiltration process, 2011, 1-5