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## Chemical Engineering Research and Design

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# Removal of copper(II) ions from aqueous solutions by complexation–ultrafiltration using rotating disk membrane and the shear stability of PAA–Cu complex

Shu-Yun Tang, Yun-Ren Qiu\*

School of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China

## ARTICLE INFO

## Article history:

Received 9 January 2018

Received in revised form 13 May 2018

Accepted 21 June 2018

Available online 28 June 2018

## Keywords:

Shear rate

Shear stability

Shear induced dissociation

Complexation–ultrafiltration

Rotating disk membrane

## ABSTRACT

The stability of polymer–metal complex in the shear field is of great significance for the industrial application of complex–ultrafiltration. The shear stability of PAA–Cu complex was investigated for the first time. Polyacrylic acid sodium (PAAS) was applied to remove Cu(II) from aqueous solutions by complexation–ultrafiltration using a rotating disk membrane. As important factors, solution pH and P/M (the mass ratio of polymer to metal ions) on the rejection of Cu(II) were investigated, and the rejection of Cu(II) could reach 99.6% at pH = 6.0, P/M = 25. The rotating disk was applied to generate shear rate on the membrane surface, and the radial distribution of shear rate on the membrane surface was calculated. The critical rotating speeds at which the rejection of Cu(II) begins to decrease were 1000, 900, 700 rpm at pH values 6.0, 5.0, 4.0, respectively, and the corresponding critical shear rates ( $\gamma_c$ ) at which the PAA–Cu complex begins to dissociate were  $8.0 \times 10^4$ ,  $6.6 \times 10^4$  and  $4.2 \times 10^4$  s<sup>−1</sup>, respectively. Furthermore, the critical shear radius and the radial distribution of substances on the membrane surface were obtained using a segmentation model. The shear stability, especially the critical shear rate of the polymer–metal complex, can give guidance to the selection of the delivery pumps so that high removal efficiency can be obtained in the industrial application of complexation–ultrafiltration. In addition, shear induced dissociation and ultrafiltration was first applied to regenerate PAAS.

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## 1. Introduction

Heavy metals pollution in natural waters caused by metal plating industry has aroused general attention in last few decades. Metal plating wastewater streams contain a large amount of Cu(II) (Castelblanque and Salimbeni, 2004; Qin et al., 2002). Cu(II) shows moderate toxicity to human and animals (Álvarez-Ayuso et al., 2003; Lo et al., 2012). Cu(II) causes serious problems to human such as stomach intestinal distress, kidney damage, anemia and even coma and eventual death (Molinari et al., 2008). The World Health Organization (WHO) recommends a level of copper in the drinking water below 2 mgL<sup>−1</sup> (Gorchev and Ozolins, 2011). A number of methods have been proposed for

the removal of Cu(II). As previously reported, chemical precipitation, adsorption and ion-exchange are some of the most commonly used processes, but there exist the disadvantages, such as metals recovering difficulty, high-energy requirements and production of sludge (Ahmed Basha et al., 2013; Awual et al., 2013; Cheng, 2006; Fu and Wang, 2011; Petrov and Nenov, 2004; Rahman and Islam, 2009).

Complexation–ultrafiltration, also called polymer enhanced ultrafiltration or polymer assisted ultrafiltration, is one of the most promising methods in the treatment of wastewater containing heavy metals with significant advantages, like low-energy requirements, high removal efficiency (Camarillo et al., 2010; Cañizares et al., 2005; Zeng et al., 2009). In that process, the metal ions are firstly bound to polymers to form macromolecular complex and rejected by membrane, whereas unbound metal ions pass through the membrane. Some water soluble polymer complexing agents, such as polyacrylic acid sodium (PAAS), polyetherimide (PEI) and acrylic acid–maleic acid copolymer

\* Corresponding author.

E-mail address: [csu.tian@csu.edu.cn](mailto:csu.tian@csu.edu.cn) (Y.-R. Qiu).<https://doi.org/10.1016/j.cherd.2018.06.030>

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## Nomenclature

### Roman letters

|            |                                                                                                                    |
|------------|--------------------------------------------------------------------------------------------------------------------|
| $C_f$      | initial Cu(II) concentration (mgL <sup>-1</sup> )                                                                  |
| $C_0$      | Cu(II) concentration in permeate at rest (mgL <sup>-1</sup> )                                                      |
| $C_p$      | Cu(II) concentration in permeate (mgL <sup>-1</sup> )                                                              |
| $C_r$      | Cu(II) concentration in retentate (mgL <sup>-1</sup> )                                                             |
| $C_{com}$  | Cu(II) concentration in permeate of the complexation region (mgL <sup>-1</sup> )                                   |
| $C_{dis}$  | Cu(II) concentration in permeate of the dissociation region (mgL <sup>-1</sup> )                                   |
| $F$        | permeation coefficient (L m <sup>-2</sup> h <sup>-1</sup> kPa <sup>-1</sup> , m s <sup>-1</sup> Pa <sup>-1</sup> ) |
| $J$        | permeate flux (L m <sup>-2</sup> h <sup>-1</sup> , m s <sup>-1</sup> )                                             |
| $k$        | velocity following factor                                                                                          |
| $N$        | rotating speed (rpm)                                                                                               |
| $N_c$      | critical rotating speed (rpm)                                                                                      |
| $P$        | pressure on the membrane surface (kPa)                                                                             |
| $\Delta P$ | transmembrane pressure (kPa)                                                                                       |
| $r_m$      | outsider radius (m)                                                                                                |
| $r_0$      | insider radius (m)                                                                                                 |
| $r_c$      | critical radius (m)                                                                                                |
| $R_{Cu}$   | rejection of Cu(II) (%)                                                                                            |
| $R_t$      | total resistance (m <sup>-1</sup> )                                                                                |
| $R_m$      | membrane intrinsic resistance (m <sup>-1</sup> )                                                                   |
| $R_f$      | fouling resistance (m <sup>-1</sup> )                                                                              |
| $R_c$      | concentration polarization resistance (m <sup>-1</sup> )                                                           |
| $t$        | time (h)                                                                                                           |
| $V_p$      | permeate volume (L)                                                                                                |
| $V_m$      | make-up water volume (L)                                                                                           |
| $V_{com}$  | permeate volume of complexation region (L)                                                                         |
| $V_{dis}$  | permeate volume of dissociation region (L)                                                                         |

### Greek letters

|            |                                                       |
|------------|-------------------------------------------------------|
| $\mu$      | dynamic viscosity (Pa s)                              |
| $\nu$      | kinematic viscosity (m <sup>2</sup> s <sup>-1</sup> ) |
| $\rho$     | fluid density (kg m <sup>-3</sup> )                   |
| $\gamma_c$ | critical shear rate (s <sup>-1</sup> )                |
| $\gamma_m$ | shear rate (s <sup>-1</sup> )                         |

(PMA-100) have been used to treat heavy metal ions in wastewater (Álvarez-Ayuso et al., 2003; Barakat and Schmidt, 2010; Li et al., 2008; Qiu and Mao, 2013). Most researchers focused on the removal efficiency influenced by the pH, mass ratio of polymer to metal and background electrolytes with various complexing agents, and the optimum operation parameters were obtained (Ennigrou et al., 2015; Juang and Chiou, 2000; Korus and Loska, 2009; Molinari et al., 2004; Petrov and Nenov, 2004; Qiu and Mao, 2013), which is of importance for the application of complexation-ultrafiltration. Polyacrylic acid sodium (PAAS), a polymer with good water solubility and high affinity toward heavy metal ions, is widely used as a complexing agent in heavy metals treatment (Camarillo et al., 2012, 2010; Cañizares et al., 2005; Korus et al., 1999). The complexation-ultrafiltration presents great potential for the treatment of wastewater containing Cu(II) and the removal efficiency of Cu(II) is closed to 100% in laboratory (Molinari et al., 2008; Qiu and Mao, 2013). However, complexation-ultrafiltration has not yet been used in industrial scale. One of the significant reasons is due to the great declination of rejection in industrial amplified experiment, or rather, is that the polymer-metal complex loses its stability when the shear rate exceeds a certain value and the dissociated metal ions can easily pass through the membrane, and this is verified in this work.

A lot of experiments on complexation-ultrafiltration using hollow fiber membrane have been done in our previous researches (Gao et al.,

2012; Qiu and Mao, 2013), and the results reveal that the removal efficiency depends on the kinds of the delivery pumps (peristaltic pump ~100% and centrifugal pump ~45%) for the same membrane module. The similar result was obtained by the Buckley et al. (1990), they used a pilot plant to treat heavy metal in wastewater, but the removal efficiency was only ~40%, far lower than that in the laboratory. The rapid decrease of rejection may be the dissociation of the polymer-metal complex when the feed flows through the centrifugal pump with high rotating speed. The high shear rate, caused by the blades of the centrifugal pump, would destroy the bond of carboxyl-metal and lead to the dissociation of polymer-metal complex, resulting in a remarkable decline of the removal efficiency. That is to say, the polymer-metal complex may dissociate when the shear rate exceeds a certain value. That is one of the main reasons why the application of the complexation-ultrafiltration is restricted in industrialization.

To study the stability of polymer-metal complex in the shear field, a rotating disk membrane (RDM) was used to generate shear field on the membrane surface. Rotating disk membrane filtration consists in creating the shear rate on the membrane surface by a relative motion between the fixed membrane and a disk rotating (Jaffrin, 2008). RDM can yield higher permeate flux and better solute transmission than conventional cross flow filtration due to the high shear rates which can prevent or reduce the membrane fouling and concentration polarization resistance (Ding et al., 2002; Moulaï-Mostefa et al., 2007; Torras et al., 2009; Tu et al., 2009). RDM can be used to the purification and separation of various products, such as baker yeast suspensions (Brou et al., 2002), milk proteins (Akoum et al., 2006; Ding et al., 2002; Frappart et al., 2006; Luo et al., 2012, 2010), oil in water emulsions (Moulaï-Mostefa et al., 2007), anionic surfactant (Tu et al., 2009), and chicory juice (Zhu et al., 2013). However, the removal of heavy metal ions by complexation-ultrafiltration using rotating disk membrane, has been rarely reported.

In this work, the removal efficiency of Cu(II) was evaluated by complexation-ultrafiltration process using rotating disk membrane, and PAAS as complexation agent. The effects of rotating speed, polymer/metal mass ratio (P/M) and pH on the removal efficiency of Cu(II) were investigated. What is more, the stability of PAA-Cu complex in the shear field was investigated for the first time. The radial distribution of shear rate on the membrane surface was calculated, and the critical shear rate, the smallest shear rate at which the PAA-Cu complex starts to dissociate, was calculated. Furthermore, the critical shear radius and the radial distribution of substances on the membrane surface were obtained using a segmentation model. In addition, a novel recovery method, shear induced dissociation and ultrafiltration, without consumption of acid and alkali, compared with the change of pH, was successfully used to regenerate PAAS for the first time.

## 2. Experimental

### 2.1. Materials

The chemical reagents used in the experiments were poly (acrylic acid) sodium (PAAS) with average molecular weight 250 kDa (Wako Pure Chemical Industries, Ltd., Japan) and cupric chloride (CuCl<sub>2</sub>·2H<sub>2</sub>O), HCl, NaOH (analytical grade, Sinopharm Chemical Reagent Co., Ltd., China). The initial concentration of Cu(II) was 10 mg/L for all the solutions if no explanation was given. Sodium hydroxide and hydrochloric acid were used to control pH in solution. Ultrapure water (prepared by ultrafiltration and reverse osmosis) was used in the experiment. The PAAS were pretreated before use so that the shorter polymers which can pass through the membrane be eliminated. The PAAS solution was pretreated using the PES (Polyether sulfone) hollow ultrafiltration membrane (molecular weight cut-off (MWCO) 20 kDa, Tianjin Aisheng Membrane Filtration Tech. Co. Ltd, China) until no polymer was detected

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