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Removal of manganese from waste water by complexation−ultrafiltration using copolymer of maleic acid and acrylic acid

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Abstract: Copolymer of maleic acid and acrylic acid (PMA-100), combining with polyvinyl butyral (PVB) ultrafiltration membrane was used for the removal of Mn(II) from waste water by complexation−ultrafiltration. The carboxylic group content of PMA-100 and the rate of complexation reaction were measured. Effects of the mass ratio of PMA-100 to Mn(II) (n), pH, background electrolyte, etc on the rejection rate (R) and permeate flux (J) were investigated. The results show that carboxylic group content of PMA-100 is 9.5 mmol/g. The complexation of Mn(II) with PMA-100 is rapid and completed within 5 min at pH 6.0. Both R and J increase with pH increasing in the range of 2.5−7.0, and R increases with the increase of n at pH 6.0 while J is little affected. The background electrolyte leads to the decrease of R, and $CaCl_2$ has much greater effect on R than NaCl at the same ionic strength.

Key words: complexation−ultrafitration; copolymer of maleic acid and acrylic acid; poly (vinyl butyral) hollow fiber membrane; manganese; wastewater treatment

1 Introduction

Manganese is a common contaminant of mine water and other waste waters, and it can gradually be oxidized to insoluble manganic dioxide causing several problems such as water discoloration, metallic taste, odor, turbidity, biofouling and corrosion, staining of laundry. Most common methods to remove Mn(II) are oxidation and precipitation [1,2]. Complexation−ultrafiltration, also described as polymer enhanced ultrafiltration (PEUF) or polymer assisted ultrafiltration (PAUF), is one of the most promising methods in treatment of the wastewater containing heavy metals with significant advantages, like low-energy requirements, high removal efficiency and high selectivity of separation if selective bonding agents are applied [3,4]. In that process, the metals are firstly bound to polymers to form macromolecular complex and rejected by membrane, whereas unbound metals pass through the membrane [5].

Complexation−ultrafiltration process has been successfully used for the treatment of wastewater containing kinds of metal ions such as Co^{2+} [3,4], Pb^{2+} [4], Cu^{2+} [3,5,6], Cd^{2+} [7], Zn^{2+}, Ni^{2+} [8,9] and Hg^{2+} [10]. The selection of water soluble polymer is of significance in complexation−ultrafiltration process, and the natural character directly decides the efficiency of combination with target metal ions and the operation conditions required. In the previous studies, polyethyleneimine (PEI) [5,9−11] and polyacrylic acid (in its sodium PAAS or hydrogen form PAA) [8,9, 12] were most widely used. Copolymer of maleic acid and acrylic acid (PMA-100), a copolymer made of maleic acid and acrylic acid with abundant carboxyl functional groups, as shown in Fig. 1, can be used as complexing agent in complexation−ultrafiltration process [13], but has not been deeply studied as water-soluble polymer in complexation−ultrafiltration process. The high content of the carboxyl group is a significant feature and possibly corresponding to a high capacity of binding metal ions [6,14].

Complexation−ultrafiltration was firstly used for the removal of manganese from simulated waste water by using copolymer of maleic acid and acrylic acid (PMA-100) and polyvinyl butyral (PVB) hollow fiber ultrafiltration membrane. Acid−base property of the polymer was analyzed by potentiometric and

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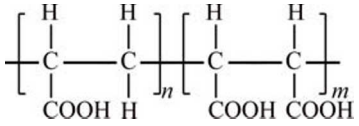

Fig. 1 Structure of PMA-100

conductimetric titrations, and the effects of polymer/metal ratio and pH etc on both rejection rate and permeate flux were studied. In addition, a comparative study of sodium chloride and calcium chloride on the effect of removal rate of manganese was also carried out.

2 Experimental

2.1 Chemicals and membrane

Copolymer of maleic acid and acrylic acid (PMA-100), with the relative molecular mass 50 kDa, supplied by Shenyang Xingqi Daily Chemicals Plant (China), was previously pretreated to eliminate the small molecular mass fractions. $MnSO_4{\cdot}H_2O$ was used as sources of Mn^{2+}. The pH of solution was adjusted by adding hydrochloric acid (0.1 mol/L) or sodium hydroxide (0.1 mol/L). All the solutions in the experiment were prepared with deionized water.

Polyvinyl butyral (PVB) hollow fiber membrane was produced via thermally induced phase separation method [15] and its main parameters are listed in Table 1.

Table 1 Main parameters of PVB hollow fiber ultrafiltration membrane

MWCO/kDa	Area/m^2	Outside/inside diameter/mm	Length/mm
20	0.31	1.10/0.64	258

2.2 Ultrafiltration experiment

The UF experiment in laboratory-scale was carried out with the apparatus shown in Fig. 2. An initial feed of 2.5 L was introduced to the feed tank and was circulated through the apparatus. Flow rate of 40 L/h and operative pressure of 40 kPa were controlled. The temperature was kept at 27 °C with the help of thermostatic water batch. In the total recirculation process, both the permeate and retentate stream were returned to the feed tank so that the concentration of feed was constant. The sample of permeate was taken for analysis.

The concentration of the permeate was analyzed by atomic absorption spectroscopy (Shi-Madzu AA-670) and the permeate flux was measured by weighing the permeate volume produced in a certain quantity of time.

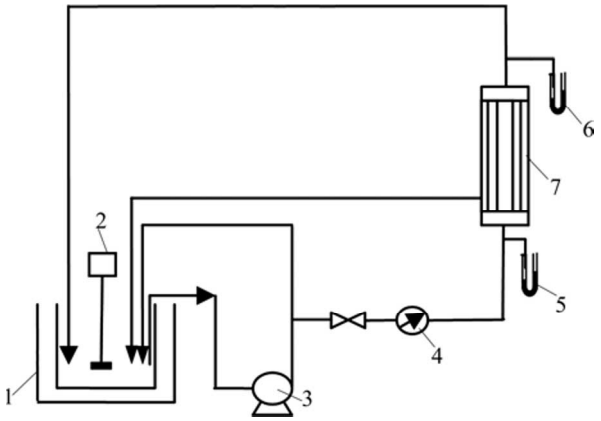

Fig. 2 Scheme of experimental apparatus: 1—Feed tank with a thermostatic bath; 2—Stirrer; 3—Pump; 4—Flow meter; 5,6—Mercury pressure meter; 7—Hollow fiber ultrafiltration membrane

2.3 Measurement of concentration of carboxylic group

15.0 mg of PMA-100 was precisely weighed and dispersed in 250 mL of deionized water (final concentration was 60 mg/L), and 0.1 mol/L HCl was added in the beginning of the experiment to lower the pH to approximately 3. Titrations were carried out by stepwise addition of 0.25 mL of 0.1 mol/L NaOH (standardized by potassium acid phthalate) to the flask placed in thermostated cell (27 °C) while the suspension was stirred under a nitrogen atmosphere. The conductivity was measured using a conductivity meter (DDS−11A, Lei-Ci) and pH of solution was recorded with a pH meter (PHS−3C, from Shanghai Precision & Scientific Instrument Co. Ltd, China). Conductivity and pH values were recorded after stabilization. The concentration of the carboxylic group can be calculated by

$$C_{\mathrm{p,COOH}} = cV / m_{\mathrm{p}} \quad (1)$$

where $C_{\mathrm{p,COOH}}$ is the content of carboxylic group (mmol/g); c is the molar concentration of NaOH added into the titration system (mol/L); V is the titrant volume up to equivalence point (mL); m_{p} is the mass of the polymer (g).

3 Results and discussion

3.1 Potentiometric and conductimetric titrations of polymer

The titration curves are shown in Fig. 3(a). Conductivity initially decreases sharply due to the neutralization of free protons coming from hydrochloric acid while solution pH slowly increases because of consumption of hydrochloric acid. When all of hydrochloric acid is neutralized, the weak acidic