Integration of ceramic membrane and compressed air-assisted solvent extraction (CASX) for metal recovery

Chi-Wang Li, Chun-Hao Chiu, Yu-Cheng Lee, Chia-Hao Chang, Yu-Hsun Lee and Yi-Ming Chen

ABSTRACT

In our previous publications, compressed air-assisted solvent extraction process (CASX) was developed and proved to be kinetically efficient process for metal removal. In the current study, CASX with a ceramic MF membrane integrated for separation of spent solvent was employed to remove and recover metal from wastewater. MF was operated either in crossflow mode or dead-end with intermittent flushing mode. Under crossflow mode, three distinct stages of flux vs. TMP (trans-membrane pressure) relationship were observed. In the first stage, flux increases with increasing TMP which is followed by the stage of stable flux with increasing TMP. After reaching a threshold TMP which is dependent of crossflow velocity, flux increases again with increasing TMP. At the last stage, solvent was pushed through membrane pores as indicated by increasing permeate COD. In dead-end with intermittent flushing mode, an intermittent flushing flow (2 min after a 10-min or a 30-min dead-end filtration) was incorporated to reduce membrane fouling by flush out MSAB accumulated on membrane surface. Effects of solvent concentration and composition were also investigated. Solvent concentrations ranging from 0.1 to 1% (w/w) have no adverse effect in terms of membrane fouling. However, solvent composition, i.e. D2EHPA/kerosene ratio, shows impact on membrane fouling. The type of metal extractants employed in CASX has significant impact on both membrane fouling and the quality of filtrate due to the differences in their viscosity and water solubility. Separation of MSAB was the limiting process controlling metal removal efficiency, and the removal efficiency of Cd(II) and Cr(VI) followed the same trend as that for COD.

Key words | ceramic membrane, dead-end filtration, recovery, solvent

INTRODUCTION

Micro-sized solvent-coated air bubbles (MSAB) generated by a novel process, compressed air-assisted solvent extraction process (CASX), were employed to remove metal ions from aqueous phase and were shown to be kinetically efficient (Li et al. 2007, 2008). Sizes of MSAB are in the range of 5–50 μm and are much larger than those of emulsified solvent droplets which have diameter of less than 3 μm (Li et al. 2008). Although separation of the metal-loaded MSAB from treated water can be achieved relatively easy by mean of gravity separation compared to that of emulsified solvent droplets, applying membrane to treat MSAB-containing water is of great interested to increase the throughput of CASX process.

The application of membrane processes for oily water treatment have been extensively studied in the past (Hlavacek 1995; Cumming et al. 2000; Marchese et al. 2000; Panpanit & Visvanathan 2001; Zhao et al. 2005, 2006; Headen et al. 2006; Lobo et al. 2006; Hua et al. 2007) with the effects of membrane pore size, transmembrane pressure (TMP), crossflow velocity, oil concentration, pH, ionic...
strength, permeate flux, and particle addition on membrane fouling being investigated. Lobo et al. (2006) used two ceramic UF filters (50 and 300 kDa, Carbosep) for oil/surfactant/water separation with pressure operated at 50 to 400 kPa, indicating that increasing crossflow velocity and pH increased permeate flux. Increasing crossflow velocity decreases concentration polarization of oil on membrane surface, while increasing pH decreases surface charge of membrane (isoelectric point for this type of membrane is close to 4) as the result of increasing repulsion force between negatively charged membrane and negatively charged oil droplets. COD removal of higher than 90% was observed under all conditions tested, and the membrane with small pore size achieved higher COD removal than the membrane with big pore size. However, in their study only 20-min experimental run was conducted for each condition.

Unlike filtration of rigid particles, membrane filtration of deformable particle, such as emulsified solvent droplets or MSAB, might display a very different flux and TMP relationship compared to that of rigid particles (Koltuniewicz et al. 1995; Headen et al. 2006; Hua et al. 2007). It is possible that at elevated TMP deformable solvent droplets or MSAB might be pushed into and then out the membrane pores causing deterioration of permeate quality and decrease/increase of permeate flux. The minimum TMP to push out the deformable solvent droplets or MSAB through membrane pores has been formulated (Kocherginsky et al. 2007) and is dependent of interfacial tension between solvent and aqueous phase, the contact angle between solvent and membrane pore, and the membrane pore radius. With larger membrane pore, TMP required to push out solvent droplets through membrane is lower. On the other hand, membrane material, hydrophobic or hydrophilic, might affect the contact angel, for example, higher TMP might be required for hydrophobic than hydrophilic membrane for solvent droplets to be pushed through membrane. Koltuniewicz et al. (1995) used membranes with various pore sizes for oil separation, finding that the membrane with tighter pore size was less fouled by oil emulsion. Hua et al. (2007) reported removal of oily wastewater with ceramic membrane with pore size of 50 nm, having the effects of TMP, crossflow velocity, oil concentration, pH, and salt concentration investigated. In that study, TMP ranging from 0.05 to 0.3 MPa result in permeate flux of from around 40 to 200 L m$^{-2}$ h$^{-1}$. At TMP of high than 0.2 MPa, a big drop in TOC removal efficiency was observed which is attributed to, according to the authors, the push through of oil droplets at the elevated pressure. Meanwhile, the increase of flux due to the increases of TMP becomes smaller at TMP of higher than 0.2 MPa. A significant flux decline is caused by increasing salt concentration which has shown to affect the membrane flux (both positive and negative been reported).

In this study, filtration of MSAB and emulsified solvent droplets generated by CASX process and traditional emulsified method, respectively, was studied and compared using a ceramic micro-sized membrane. Effects of solvent concentration, solvent composition, i.e. extractant/diluent ratio, membrane flux, crossflow velocity, and membrane operation modes were investigated.

**EXPERIMENTAL SECTION**

All chemicals were of reagent grade. Synthetic wastewaters containing Cr(VI) or Cd(II) of 100 mg L$^{-1}$ were prepared from potassium chromate (Riedel-de Hae`n) or 1,000 mg L$^{-1}$ ICP standard (J. T. Baker) diluted with deionized water. Several batches of electroplating wastewaters were collected from local electroplating facility in northern Taiwan during 2004/10–2005/7 and were mixed together in this study. Table 1 showing the water quality of the collected wastewaters indicates that pH of the wastewater is quite acidic with Cr(VI) concentration in the ranges of 400–888 mg l$^{-1}$. Triocylmethyammonium chloride

<table>
<thead>
<tr>
<th><strong>Table 1</strong></th>
<th>Chemical compositions of the electroplating wastewater</th>
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<tr>
<td>pH</td>
<td>Cr$^{6+}$</td>
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<td>1.2–2.4</td>
<td>400–887$^+$</td>
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$^*$ Concentration (mg L$^{-1}$).
(Aliquat 336; ACROS) and Bis(2-ethylhexyl) hydrogen phosphate (D2EHPA; Fluka) were employed as the metal extractants (Li et al. 2008), and kerosene (CPC Corporation, Taiwan) purchased from local gas station was chosen as the organic diluent. Various weight ratios of extractant/kerosene (denoted as solvent) mixtures were prepared before experiments.

Figure 1 shows the schematic setup of the proposed process. The solvent tank was made of stainless steel. After equilibrium at the desired pressure for at least 5 min, pressurized solvent was then released to a glass column reactor (I.D. of 6 cm; height of 50 cm) housing 500 ml of metal-containing aqueous solution (pre-equilibrated in a 25°C water bath), generating MSAB. The aqueous phase was allowed to react with MSAB for pre-determined time under gentle aeration (0.6 L min⁻¹). A multi-channel ceramic membrane tubular module (Kerasep™, Rhodia Orelis) having length of 390 mm, external diameter of 25 mm, and pore size of 0.1 μm is housed in clear acrylic pipes. With seven channels and diameter of 6 mm for each channel, the membrane has effective area of 0.052 m². Emulsified solvent-containing wastewater was also prepared by traditional method using a centrifugal pump under very high flow velocity of 50 L min⁻¹ for 30 min.

Membrane was operated in two modes, namely cross-flow mode and dead-end with intermittent flushing mode. Permeate flux and TMP were both recorded by a laptop computer connecting to an electronic balance and two pressure gauges installed in the inlet and outlet of the membrane module. In dead-end with intermittent flushing mode, flushing pump was turned on for 2 min to flush out solvent accumulated inside membrane (crossflow velocity of 1 L min⁻¹) after a certain interval (10 or 30 min). After each test, membrane was cleaned by circulating 1% of detergent (1 L) for 30 min, followed by backwashed with 3 L of DI water under TMP of 103 kPa. Membrane was further cleaned by circulating 0.3% of HNO₃ (1 L) for 60 min, followed by backwashed again with 3 L of DI water (TMP of 103 kPa).

Concentration of Cd(II) was analyzed by a flame atomic absorption spectrometry (Hitachi Z6100, Hitachi, Tokyo, Japan). Cr(VI) was analyzed colorimetrically according to the standard method 3500B, and COD was analyzed followed the standard method 5520C (APHA 1998). Samples for Cr(VI) analysis were filtered immediately under vacuum through a 1.2 μm GF/C glass microfiber filter paper (Whatman, Middlesex, UK) and then 0.45 μm cellulose acetate filter paper (Advantec MFS, Pleasanton, USA). Samples with elevated COD were further filtered with a hydrophilic UF membrane (YM10, Millipore, USA) having a MWCO of 10 kDa in a batch stirred cell (Amicon 8,200 stirred cell, Millipore, USA) at 100 rpm. The applied pressure was controlled at 207 kPa (30 psi) using compressed nitrogen gas.
RESULTS AND DISCUSSION

Separation of solvent by membrane in the crossflow mode

Separation of solvent from MSAB-containing water under crossflow filtration mode with various crossflow velocity was compared using initial solvent concentration of 0.4% (w/w), D$_2$EHPA/Kerosene ratio of 1:10 (w/w), and pH = 4.0. Three distinct stages of flux/COD vs. TMP relationship are found as indicated in Figure 2. In the first stage, flux increases with increasing TMP which is followed by the stage of relatively stable flux with increasing TMP. After reaching a threshold TMP which is dependent of crossflow velocity, flux increases again with increasing TMP. At this stage, solvent was pushed through membrane pores as indicated by increasing permeate COD and simultaneous increase of permeate flow rate.

As indicated previously, solvent droplets or MSAB are deformable particles which might have very different flux and TMP relationship compared to that of rigid particles when filtered by membrane (Koltuniewicz et al. 1995; Headen et al. 2006; Hua et al. 2007). At elevated TMP deformable solvent droplets or MSAB are pushed into and then out the membrane pores, causing deterioration of permeate quality and increase of permeate flux. It is interested to note that higher crossflow velocity caused the push out of MSAB through membrane pores at lower TMP. The reason might be that at high crossflow rate the fouling layer of solvent is much thinner than that at low crossflow rate, resulting in less pressure drop across this fouling layer and allowing solvent push through the membrane pores at lower TMP. It is also possible that at low crossflow velocity, coalescence of MSAB is more pronounced than that at high crossflow velocity, resulting in higher TMP needed to push out MSAB.

The removal efficiency of Cd(II) is also shown in Figure 2(b), revealing that the removal efficiency follows the same trend as that for COD. This is not unexpected. As indicated in our previous study (Li et al. 2008), CASX is a very efficient process for extracting metal from aqueous phase to solvent phase, i.e. MSAB. Therefore, completed COD retention by membrane is coincident with completed Cd(II) retention, and the breakthrough of COD is resemble with that of Cd(II).

It is noted that during these tests MSAB was further emulsified by crossflow pump, making MSAB resemble to emulsified solvent droplets. As indicated earlier (Li et al. 2008), MSAB is quite different in both size and density from emulsified solvent droplets. To avoid the possibility of creating emulsified solvent droplets by crossflow pump, the membrane system was then operated in dead-end filtration with intermittent flushing mode.

Separation of solvent by dead-end with intermittent flushing mode

Comparison of solvent-coated air bubbles and emulsified solvent separation

Since higher crossflow caused solvent breakthrough at lower TMP and during crossflow operation MSAB was
further emulsified by crossflow pump, dead-end filtration with intermittent flushing mode was tested in the section. The dead-end filtration is becoming popular for the purpose of reducing energy cost associated to crossflow pumping (Judd & Hillis 2001; Lee et al. 2005). In this section, separation of MSAB and emulsified solvent by dead-end filtration was compared. As indicated in Figure 3(a), TMP for system treating MSAB is quite steady throughout the run but is gradually increasing for system treating emulsified solvent droplets. Permeate COD are in the range of 60 to 140 mg L\(^{-1}\), and with COD of around 4,100 mg L\(^{-1}\) in feed solution the removal efficiencies are in the range of 96 to 99% (see Figure 3(b)).

**Effect of solvent concentration and solvent composition**

Effect of solvent content ranging from 0.1 to 1% (w/w), i.e. 1 to 10 g of solvent per L of water, was tested.

As indicated in Figure 4(a) the initial TMP is different under different conditions, however, the variation is very small (~3 kPa). It is the combining effects of the extent of membrane cleaning and the relative position of inlet, outlet, and membrane. Nevertheless, TMP of these systems are quite stable throughout the test. On the other hand, solvent composition does show impact on the TMP. As indicated in Figure 4(b), increasing extractant concentration with solvent content fixed at 0.4% does increase the TMP gradually with filtration time. Increasing extractant concentration, e.g. D\(_2\)EHPA/kerosene ratios of 1:1 and 5:1, increases solvent viscosity which in terms increasing membrane fouling. Meanwhile, COD of filtrate (data not shown) is less than 160 mg L\(^{-1}\) from systems treating various solvent contents under fixed D\(_2\)EHPA/kerosene ratio of 1:10. However, COD increases from less than 160 mg L\(^{-1}\) for treating D\(_2\)EHPA/kerosene ratio of 1:10 to around 600 mg L\(^{-1}\) for systems treating D\(_2\)EHPA/kerosene
ratio of 5:1, indicating that D$_2$EHPA is released from solvent phase to aqueous phase.

The effect of metal extractants is investigated using Aliquat 336, which is used in this study for Cr(VI) removal. As indicated in Figure 5(a), TMP is in the ranges of 20 to 30 kPa, which is higher than those for the systems treating D$_2$EHPA. It is expected, understanding that Aliquat 336 has viscosity of 50 to 60 times higher than that of D$_2$EHPA. Meanwhile, COD of filtrate is breakthrough sharply after 30 min of run time.

Figure 5(b) is the COD profile of the same system operated under lower flux (15 L m$^{-2}$ hr$^{-1}$) than that in Figure 5(a), indicating that time of COD breakthrough is prolonged (to around 80 min) with lower flux. It was then decided to incorporate backwashing (with filtrate under back-pressure of 100 kPa) along with flushing into the system. As indicated in the figure, no significant COD breakthrough during more than 4 hr of test. The relatively high COD for filtrate of Aliquat 336 than that of D$_2$EHPA is related to the solubility of these two extractants in aqueous phase.

Since samples for Cr(VI) analysis have to be pretreated by filtration to remove MSAB before they can be analyzed colorimetrically, the Cr(VI) removal efficiency is always 100% after sample pretreatment. In fact, the Cr(VI) removal in the permeate should be resemble with that of COD. As indicated above, CASX is quite efficient in metal removal. With adequate solvent dosage, all Cr(VI) ions were extracted into MSAB, and separation of MSAB will be the limiting process controlling metal removal efficiency. Thus, COD removal efficiency should be use as the surrogate for Cr(VI) removal.

**CONCLUSIONS**

Integration of CASX and a ceramic MF membrane was employed to remove and recover metal from wastewater. MF was operated either in crossflow mode or dead-end with intermittent flushing mode. Under crossflow mode, three distinct stages of flux vs. TMP relationship were observed. Since higher crossflow caused solvent breakthrough at lower TMP and during crossflow operation MSAB was further emulsified by crossflow pump, dead-end filtration with intermittent flushing mode was tested. In dead-end with intermittent flushing mode, an intermittent crossflow was incorporated to reduce membrane fouling by flush out solvent accumulated on membrane surface. Solvent concentrations ranging from 0.1 to 1% (w/w) have not detrimental effect on membrane fouling. However, solvent composition showed impact on membrane fouling. TMP increased with increasing filtration tim for systems treating solvent-containing water made of extractant/diluent ratios of 1:1 and 5:1. Aliquat 336 has significant impact on both membrane fouling and the quality of filtrate due to its high viscosity and water solubility. To overcome the impact of viscosity, backwashing step is incorporated along with flushing for system treating Aliquat 336. CASX alone is a very efficient process for extracting metal from aqueous phase to solvent phase, i.e. MSAB. Therefore, separation of MSAB was the limiting process controlling metal removal efficiency. Completed COD retention by membrane is
coincident with completed Cd(II) retention, and the removal efficiency of Cd(II) and Cr(VI) followed the same trend as that for COD.

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