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Removal of cobalt ions from simulated radioactive wastewater by vacuum membrane distillation

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ABSTRACT

The separation of cobalt ions (Co^{2+}) by vacuum membrane distillation (VMD) process with commercial polypropylene hollow fibers membrane was investigated. The effect of operational parameters, including feed temperature (30–70 °C), permeate vacuum degree (0.10–0.98 atm) and feed flow rate (10.5–41.8 L/h), on the membrane flux was examined. The Pearson correlation analysis was employed to evaluate the significance of different operating parameters to the permeate flux. The results showed that permeate vacuum was the most significant to membrane flux (Pearson correlation coefficient = 0.621). The mass transfer mechanism during Co^{2+} separation was analyzed and Knudsen diffusion was proved to be the dominant mass transfer mechanism during VMD process. Dusty gas model could estimate the membrane flux well with average relative error of 5.21%. VMD method has shown its potential in the treatment of cobalt-containing wastewater.

1. Introduction

The radioactive wastewater treatment is becoming more and more important as the rapid development of nuclear power plants in China in recent years. Cobalt ions are usually existed in radioactive wastewater (Nishad et al., 2012; Wang and Chen, 2014). In addition, ^{60}Co is also widely used in medical field and industry (Omar et al., 2009)[2], which has high energy gamma radiation (2.5 MeV) and relatively long half-life period ($T_{2/1}$ 5.27a). Different technologies, especially adsorption and membrane technology, have been studied for the removal of Co from aqueous solution (Wang and Chen, 2006; Mizera et al., 2007; Chen and Wang, 2008, 2010; Kumbasar, 2009; Omar et al., 2009; Wang and Chen, 2009; Nishad et al., 2012; Zhu et al., 2012, 2014; Xing et al., 2016; Xing and Wang, 2016). There were several adsorbents, including carbon materials based adsorbents (Mizera et al., 2007; Nishad et al., 2012), mineral based adsorbents (Omar et al., 2009), biosorbents (Chen and Wang, 2008, 2012), and the like.

Bhaskarapillai et al. (2009) firstly reported a polymeric adsorbent capable of specific removal of cobaltous ions in the presence of large excess of ferrous ions, which could be used to significantly reduce the radioactive waste volume generated during decontamination of nuclear reactors. They found that the imprinted polymer could selectively and rapidly trap even when present in ppb levels from strong complexing medium against excess ferrous ions. This adsorbent is promising in selectively removing cobalt(II) ions, which can indeed help reduce the volume of the radioactive waste to a high degree.

Various membrane types were applied for the removal of Co^{2+}, including ultrafiltration (Kim et al., 2005; Zakrzewska-Trznadel et al., 2009), nanofiltration (Bouranene et al., 2008; Gherasim et al., 2015)[8, 10], reverse osmosis (Sylvester et al., 2013; Jia et al., 2016), membrane distillation (Khayet, 2013; Liu and Wang, 2013; Zakrzewska-Trznadel et al., 1999), etc. Compared with adsorption method, membrane technology has advantages of high salt rejection efficiency and high wastewater concentration factor. However, most of membrane technologies are pressure-driven. Membrane distillation (MD) process uses temperature difference instead of pressure difference as mass transfer driving force (Lawson and Lloyd, 1997). In our previous work, we found that the radionuclide removal efficiency of MD process could be over 99%. MD process has several advantages over pressure-driven membrane process: high salt removal efficiency, less membrane fouling, lower operation pressure, safer during operation, free from the influence of osmotic pressure and ability of employing low quality heat sources like industrial waste heat and solar heat as driving force (Lawson and Lloyd, 1997; Liu and Wang, 2016; Zuo et al., 2016).

VMD is based on the temperature-driven process, which is efficient method and especially suitable for the treatment of radioactive wastewater, because there is surplus heat produced in Nuclear Power Plant, which can be used by VMD process for heating the wastewater (Jia et al., 2017). There are three main configurations for VMD membrane: flat sheet, spiral wound and hollow fiber (El-Bourawi et al., 2006).

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Nomenclatures

A	Total effective membrane area (m^2)
ARE	Average relative error
σ_i	Gas molecular collision diameter (m)
DCMD	Direct contact membrane distillation
d	Hydraulic diameter (m)
DGM	Dusty gas model
d_p	Membrane average pore diameter (m)
Δm	Mass increase of the permeate collected in the condense (g)
ΔP	pressure difference across the membrane surface (Pa)
Δt	Sampling time (h)
Δ	Membrane thickness (m)
ε	Membrane porosity
J	Permeate flux ($L \cdot m^{-2} \cdot h^{-1}$)
$\overline{P}$	Average value of permeate flux ($L \cdot m^{-2} \cdot h^{-1}$)
J_{exp}	Actual permeate flux ($L \cdot m^{-2} \cdot h^{-1}$)
J_{DGM}	Simulated permeate flux ($L \cdot m^{-2} \cdot h^{-1}$)
k_B	Boltzmann constant ($1.380\ 10^{-23}$ J/K)
Kn	Knudsen number
λ_i	Gas molecular mean free path (m)
μ	Viscosity of feed flow ($m \cdot s \cdot g^{-1}$)
MD	Membrane distillation
P	Mean pressure in membrane pores (Pa)
P_c	Water vapor partial pressure on a convex surface (Pa)
P^{sat}	Pure water vapor saturated pressure (Pa)
ρ	Density of permeate solution in the present study ($kg \cdot L^{-1}$)
PP	Polypropylene
r	Average pore radius (m)
R	Universal gas constant (8.314 J $mol^{-1} \cdot K^{-1}$)
RO	Reverse osmosis
T	Mean temperature in membrane pores (K)
T_f	Temperature of feed side (K)
$T_{f,m}$	Temperature of membrane surface in feed side (K)
T_p	Temperature of permeate side (K)
$T_{p,m}$	Temperature of membrane surface in permeate side (K)
τ	Pore tortuosity of membrane
UF	Ultrafiltration
v	Flow velocity ($m \cdot s^{-1}$)
VMD	Vacuum membrane distillation
γ_c	Surface tension of the liquid
$\overline{x}$	Average value of operating parameter

Among them, hollow fiber membrane has the highest surface density area due to its no need of supporting materials (Lawson and Lloyd, 1997; El-Bourawi et al., 2006). This increases commercial potential of hollow fiber VMD membrane for its more compact configuration. Previous researches have studied treatment of radioactive wastewater by hollow fiber VMD method (Wen et al., 2016; Jia and Wang, 2017), studies have found VMD method was an efficient method in nuclides removal. However, the study about mass transfer mechanism during Co^{2+} separation by VMD was limited.

The objective of this study was to investigate the separation of Co^{2+} from aqueous solution by hollow fiber VMD method, to examine the mass transfer mechanism during Co^{2+} separation and the influence of operating parameters on membrane flux.

2. Materials and methods

2.1. Chemicals and membrane modules

$Co(NO_3)_2$ (Hongyan, Tianjin, China; analytical pure) was used to prepare the simulated radioactive wastewater. It is worth noting that the typical concentration of cobalt in a nuclear effluent is in ppb levels, however the concentration used in this investigation was in the range of 10 ppm. There are two main reasons: one is related to the analytical method, because it is too difficult to measure the Co^{2+} concentration in ppb levels accurately; that is to say, it could not be done due to the limitation with the detection limits of the method used. We have carried out the comparative study using the actual radioactive wastewater with or without addition of Sr^{2+}, Co^{2+} and Cs^{+} in ppm level in Nuclear Power Plant, and found that the results are consistent.

Commercial polypropylene (PP) hollow fiber membrane (Wochi, WHPP96-21, China) was used for its high hydrophobicity performance and low price. The main characteristics of the membrane module are listed in Table 1.

2.2. Experimental set-up

Fig. 1 is the flow diagram of the experimental set-up. The whole system consists of the hollow fiber MD module, feed tank, peristaltic pumps, thermostat, vacuum pump system, condenser filled with chilled water, precision balance, flowmeter and probe thermometers (Jia and Wang, 2017).

2.3. Analytical methods

Co concentration was analyzed by flame atomic absorption spectrometer (Hitachi, ZA3000, Japan). The permeate mass was determined by water mass collected in the condenser with the balance.

The membrane flux was calculated as follows:

$$J = \frac{\Delta m}{\rho A \Delta t} \tag{1}$$

where J is membrane flux ($L \cdot m^{-2} \cdot h^{-1}$); Δm is water mass collected in the condense (g); ρ is the density of permeate solution ($g \cdot m^{-3}$); A is membrane area (m^2); Δt is sampling interval (h).

3. Theoretical analysis

3.1. Mass transfer during VMD

During VMD process, there are mass and heat transfer simultaneously (Fig. 2). It could be seen that a boundary forming between the bulk solution and membrane, ascribing to the permselectivity of the membrane (Lawson and Lloyd, 1997).

During VMD mass transfer, there are two kinds of mass transfer resistance. The first resistance exists in liquid phase (Lawson and Lloyd, 1997), due to the existence of the boundary layer as result of concentration polarization of the solution. Due to the hydrophobic property of VMD membrane, liquid would be prevented from permeating through membrane. Only volatile materials in gas phase like water vapor were permitted to pass through the membrane.

When water vapor permeated through the membrane, non-volatile

Table 1
Characteristics of the VMD membrane module.

Index	Units	Value
Mean pore diameter	μm	0.18
Porosity	–	60%
Effective membrane length	mm	140
Outer radius of the fiber	mm	1.36
Inner radius of the fiber	mm	0.50
Number of hollow fibers	–	140
Total effective inner area	m^2	0.062
Packing density	–	0.35