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Separation of ammonia from radioactive wastewater by hydrophobic membrane contactor

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ABSTRACT

The radioactive wastewater produced in the manufacturing process of UO_2 kernel for high temperature gas-cooled reactor (HTR) contains high concentration of ammonia. The ammonia has to be removed effectively for further treatment of the wastewater. In this study, the hydrophobic membrane contactor (HMC) was adopted to remove and recover the ammonia from radioactive wastewater at room temperature. The operating parameters such as feed velocity and initial ammonia concentration were determined. In addition, the effect of wastewater composition on ammonia separation was studied. The experiment results showed that ammonia removal efficiency could reach above 90% after 120 min operation when pH was not adjusted. While the initial pH of wastewater was adjusted to 12.0, ammonia removal efficiency could reach above 95%. The ammonia mass transfer coefficient increased with increase of feed velocity and tended to an asymptotic value when the feed velocity reached 0.049 m/s. When the initial ammonia concentration was 2211.6 mg/L, 5864.6 mg/L and 23,898.7 mg/L, the ammonia removal efficiency was 95.0%, 94.2% and 94.1%, respectively after 120 min operation, i.e. the initial concentration of ammonia in wastewater had almost no effect on ammonia separation. In addition, the coexisting substances, such as urea and tetrahydrofurfuryl alcohol (THFA), also had no effect on ammonia separation. The HMC is a promising way to separate ammonia from radioactive wastewater.

1. Introduction

High temperature gas-cooled reactor (HTR) as an advanced type of nuclear reactor has been researched and developed by our institute since the middle of 1970s. And an HTR nuclear power plant is being constructed in Shandong province of China. For HRT the UO_2 kernel was produced by a method called total gelation processing (Tang et al., 2000, 2002). Firstly mixing up a urea and acid-deficient uranyl nitrate solution, and then the solution containing tetrahydrofurfuryl alcohol (THFA) and polyvinyl alcohol (PVA) was added. Spherical droplets were added into ammonia solution to form gel particles. Consequently a kind of radioactive wastewater, containing ^{238}U and high concentration of ammonia and THFA was produced in the process UO_2 kernels production (Fu et al., 2004). The radioactive wastewater must be treated effectively and safely to protect environment (Liu and Wang, 2013). However, the presence of high concentration of ammonia made the further treatment of ^{238}U more difficult. So it is essential to remove the ammonia firstly. Ammonia removal from wastewater is usually achieved by biological treatment when the ammonia concentration is relatively low. Air/steam stripping method is most often used for treating high concentration of ammonia in wastewater since the high concentration of ammonia will inhibit the biological nitrification process (Ashrafizadeh and Khorasani, 2010; Basakçilardan-Kabakci et al., 2007; Bonmatí and Flotats, 2003; Carrera et al., 2003). In addition, other methods such as break-point chlorination (Zhang et al., 2015), absorption (Sarioglu, 2005; Singh and Prasad, 1997), ion exchange (Jorgensen and Weatherley, 2003) and chemical precipitation were also used for ammonia removal from wastewater. However, all these technologies have their disadvantages or limitations, including the high cost, low efficiency, difficult maintenance, restricted by slow bioconversion and unfavorable environmental factors (Ashrafizadeh and Khorasani, 2010; Tan et al., 2006). So it is important to find a more efficient and economical process to remove ammonia, especially for high concentration of ammonia.

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The hydrophobic membrane contactor (HMC) employs hydrophobic micro-porous membrane (Han et al., 2005), which can separate the volatile species from aqueous solution. The hydrophobic membrane is also called gas membrane due to that the membrane pores are filled with air even when the two sides of the membrane are filled with aqueous solutions (Imai et al., 1982; Shen et al., 2006). The volatile species evaporate from aqueous solution, transfer through the membrane and then reached the striping solution, and the water and nonvolatile compounds are constrained in aqueous solution because of the hydrophobic characteristic of membrane. To increase removal efficiency the striping solution usually contains chemical compounds which can react with the volatile species. The HMC have been used to remove many kinds of volatile components from aqueous solution, such as ammonia, cyanide, hydrochloric acid, hydrogen sulfide and carbon dioxide (Gabelman and Hwang, 1999; Kenfield et al., 1988; Shen et al., 1997; Yeon et al., 2003; Wu et al., 2011a, 2011b; Zhu et al., 2005; Nosratinia et al., 2014). Imai et al. (1982) investigated the application of HMC to separate the ammonia from aqueous solution by different kinds of membrane modules. The HMC has several advantages compared with traditional physical–chemical methods and biotechnologies for ammonia removal, such as high concentration of ammonia can be treated directly; no secondary pollutants are produced; ammonia can be recovered and reused; energy requirements and capital cost are relatively low; larger interfacial area could be available per unit volume, and the equipment is convenient to operate (Tan et al., 2006; Xu et al., 2005).

The objective of this study was to investigate the removal of ammonia from radioactive wastewater using hollow fiber hydrophobic membrane contactor. The effect of co-existing substances on ammonia removal and the operating parameters were also studied.

2. Theoretical analysis

The HMC employs a hydrophobic membrane to separate the volatile species from aqueous solution. The feed solution is on one side of the membrane while striping solution is on the other side. It is generally recognized that three steps are needed to accomplish HMC (Shen et al., 1997). First, the volatile substances diffuse through the boundary layer (liquid film) from the feed; then go through the membrane pores which filled with air (gas); At last, the volatile substances were absorbed by striping solutions which usually contain substances could react with the separated pollutants. Fig. 1 shows the ammonia removal and recovery process from wastewater.

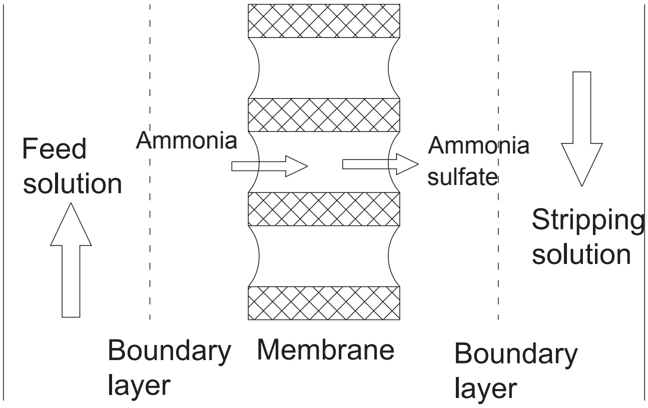

Fig. 1. Schematic representation of NH_3 removal by HMC.

As described in Fig. 1, firstly, NH_3 transfers through the air–liquid interface from wastewater and into membrane pores; then transfers through membrane pores driven by pressure difference and arrives at air–liquid interface at the stripping side; finally, NH_3 immediately reacts with H_2SO_4 to form $(NH_4)_2SO_4$ which is nonvolatile. Therefore, ammonia is removed and recovered from the wastewater.

Because the membrane absorption process involves the volatile components transferring from one phase into another, the mass transfer resistance must be discussed. Most researchers investigated the overall mass transfer resistance in HMC using the following resistance-in-series model (Hasanoğlu et al., 2010; Kenfield et al., 1988; Xu et al., 2005):

$$1/K = 1\Big/K_f + 1/K_m + 1/K_s \tag{1}$$

where, K, K_f, K_m, and K_s are the mass transfer coefficient of overall, feed side, membrane, and stripping side, respectively. Corresponding to the mass transfer rates, $1/K$, $1/K_f$, $1/K_m$, $1/K_s$ are the mass transfer resistances of overall, feed side, membrane, and stripping side, respectively.

Since the reaction of NH_3 and H_2SO_4 belongs to acid–base neutralization, the reaction rate is very quick. Consequently the NH_3 concentration in the stripping solution is nearly zero. This implies that the stripping solution did not affect the process of NH_3 absorption when H_2SO_4 in the striping solution is excessive sufficiently. In other words, the value of $1/K_s$ is small and could be ignored comparing with $1/K_f$ and $1/K_m$. As a result, the mass transfer resistances of NH_3 in HMC are mainly caused by resistances of the feed side and the membrane, therefore Eq. (1) could be simplified as follows (Hasanoğlu et al., 2010):

$$1/K = 1\Big/K_f + 1/K_m \tag{2}$$

In addition, the next equilibrium could be observed in aqueous solution containing ammonia:

$$NH_3 + H_2O \leftrightharpoons NH_4^+ + OH^- \tag{3}$$

In which K_b is the equilibrium constant, defined as follows:

$$K_b = \frac{C_{NH_4^+} C_{OH^-}}{C_{NH_3}} \tag{4}$$

$$C_t = C_{NH_3} + C_{NH_4^+} \tag{5}$$

In which C_t is the total concentration of ammonia and ammonium, and C_{NH4+} and C_{NH3} are ammonium and ammonia concentrations in solutions. $K_b = 1.8 \times 10^{-5}$ when temperature is 298 K (EL-Bourawi et al., 2007; Rezakazemi et al., 2012).

For determining the overall mass transfer coefficient, the following equation was adopted (Ashrafizadeh and Khorasani, 2010; Kenfield et al., 1988; Xu et al., 2005; Zhu et al., 2005):

$$K = \frac{V}{At} \ln \frac{C_0}{C_t} \tag{6}$$

where C_0 and C_t are the initial concentration and the instantaneous concentration at time t, A is membrane area, and V is the volume of feed solution. The value of K can be calculated from the curve of ln (C_0/C_t) versus t.

When the feeding side and stripping side have different solute concentrations, water will also evaporate from the surface of the solution with lower concentration (Gostoli, 1999), the vapor passes through the pores of the membrane and condenses on the surface