A study on the PP hollow fiber membrane contactor and its performance for removing ammonia from wastewater or mixed gas: II. Ammonia removal from mixed gas

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Abstract

In this paper, we briefly discussed the utilization of the PP HFM contactor for removal of gaseous ammonia directly from mixed gas in ammonia manufacture in order to find an economic way to substitute conventional soft-water washing absorption technology. The Hollow Fiber Membrane (HFM) contactor has very high elimination (99.9%) under optimum operation conditions. 5.1 Nm³/(m².h) gas treatment ability can be achieved, as outlet and inlet ammonia concentration are 0.02 g/Nm³ and 20.0 g/Nm³ respectively and gas stay-time in the contactor is only 0.04 s when acid supply around the membrane is sufficient. The results of industrial tests indicated that this technology could be used to eliminate mixed gas containing ammonia and replace conventional soft-water washing and absorption techniques.

Keywords

Ammonia removal; mixed gas; polypropylene hollow-fiber membrane

Introduction

There are lots of mixed gases containing ammonia in a chemical factory, such as from ammonia production, vitamin synthesis, etc. Here we emphasise on the regenerated gas from copper-washing liquid in an ammonia production factory. Commonly, the regenerated gas, in which the concentration of ammonia is usually ranged from 3 to 10 (v/v)%, is a composite of carbon monoxide, ammonia, less nitrogen, carbon dioxide and hydrogen. Before this part of the gas returns to the production system, ammonia must be removed.

The conventional method to remove ammonia is to wash regenerated gas with soft-water washing in a packed tower (Gluud and Jacobson, 1932; Kohl and Riesenfeld, 1985). Although this method is reliable, lots of soft-water exhaust and produce more dilute ammonia wastewater. As mentioned in our last paper, the wastewater containing higher concentration aqueous ammonia is not suitable to be treated by conventional biochemical technology. The wastewater is usually discharged into river or lakes directly or blow-stripped with air to release ammonia to the atmosphere again. It is very clear that, two problems exist. One is the NH₃-N environment pollution; another is the wasting of a large amount of ammonia. For example, in an ammonia synthesis factory, there are two copper-washing regeneration towers. The total 2,000 m³ (STP)/h regenerated gas is treated by soft-water washing and absorbing. Everyday about 480 tons of wastewater contain 17~25 kg/m³ ammonia discharge and 12 tons ammonia waste. In this paper we try to evaluate the feasibility of recovering ammonia from regenerated gas in a synthesis ammonia factory directly by membrane contactor.

Recently the work to remove polluted gas with a membrane contactor from mixed gas were emphasized. Jasen et al. (1994) looked at using a hydrophobic membrane contactor for CO₂ removal from flue gas in applications like ammonia production and natural gas separation. Karoor and Sirkar (1993) used a microporous polypropylene membrane contactor to study the absorption of CO₂ from CO₂/N₂ mixture. Hollow fiber microporous
membranes (HFM) were chosen to assemble the contactor because of its many advantages (Gabelman and Sun-Tak Hwang, 1999; Ho and Sirkar, 1992). This gas separation process is quite different from that taken in most other studies of membrane transport of gases, it is a “solubilization-diffusion” mechanism (Mulder, 1996). But in the membrane contactor, the gas selectivity comes from the selectivity of absorbent. Microporous membrane acting as a barrier between two phases has no selectivity. The HFM contactor offers substantial advantages compared to a packed tower. First the HFM contactor can offer larger interfacial area per unit volume than the packed tower. This increased area will make the mass transfer faster. This means we can use smaller equipment to get the same efficiency. The available membrane surface makes it possible for the fluids (gas and liquid phases) to be adjusted at high or low flow rates respectively because the both fluids are independent. In contrast, a packed tower is subjected to flooding at high flow rates and unloading at low ones. Interfacial area is known and is constant, which allow us to predict performance more easily than with a conventional mass transfer device.

In this paper, we utilize a polypropylene HF membrane contactor to remove ammonia from regenerated gas and to replace the soft-water washing and absorbing process in a synthesis ammonia factory. The NH₃ removal ability and efficiency of HFM contactor and operation conditions were carefully examined.

**Experiments**
The modules of PP HFM were fabricated by placing 4000 fibers in an ABS tube 10 cm in diameter and about 20 cm long. The total area of the module is 0.78 square metres. The module’s surface per unit volume is 876 m⁻¹. The module was sealed with epoxy resin and installed in the equipment as shown schematically in Figure 1. In experiments, the gas was passed through the fiber lumen (on the fiber side) and the absorbent (sulfuric acid) was pumped outside the fibers (on the shell size). A condenser and a magnetic force pump were attached to the reservoir for the recycling of the acid. The ammonia concentration of the mixed gas was determined by acid absorption followed by base reverse titration.

**Results and discussion**
Sulfuric acid was selected as the absorbent in this study. Its initial concentration is 4.0 N. The effect of acid concentration on ammonia removal rates was shown in Figure 2a. The ammonia concentration of inlet regenerated gas is 20.1 g/m³, or around 3 (v/v)%. It was found that the removal rate was around 97% when mixed gas flux was 4.7 m³/h and the concentration of acid was larger than 1.0 N. As is displayed in Figure 2b, one can conveniently see how the mass transport (N) changes with the concentration of the absorbent. The mass transport is constant with the acid concentration when C_{acid} is larger than 1 N. This maybe due to the sufficient supply of the acid around the fiber at this time. Figure 2b gives the mass transport relationships in the ammonia removal process with different absorbent concentrations.

![Figure 1: Flow chart of generated gas absorbed test with HFM contactor in ammonia production factory](https://iwaponline.com/ws/article-pdf/1/5-6/195/477271/195.pdf)
transfer coefficients. The mass transfer coefficient $K$ can be calculated by Equation (1) under the assumption that the gas volume changed little after being absorbed:

$$K = F \times \ln \left( \frac{C_{\text{in}}}{C_{\text{out}}} \right) / (\pi n l d) \tag{1}$$

here $K$ is the overall mass transfer coefficient, $n$ is the root, $F$ is the mixed gas flux, $C_{\text{in}}$ and $C_{\text{out}}$ are the ammonia concentration of inlet and outlet gas respectively, $l$ and $d$ are the length and inner diameter of the fiber respectively. The two curves in Figure 2b don’t pass through the zero point. This means that even pure water has some absorbing ability, because ammonia has a high solubility in water.

The process of gas absorption is quite different to that of removing ammonia from liquid. The boundary layers were controlled by acid concentration, its flow rate, even ammonia concentration. The thickness of this layer increases with the decrease of acid concentration at the same liquid flow rate. The mass transfer coefficient $K$ increases with the increase of acid concentration when the concentration is lower than 2.0 N.

Figure 3a shows that the ammonia removal rates decreases slightly with the increase of ammonia concentration. The outlet ammonia concentrations increase rapidly, but the absolute mass transport increases a great deal with the inlet concentration in the range from 20 g/Nm$^3$ to 90 g/Nm$^3$. Although overall mass transfer coefficient $K$ deceases (Figure 3b), the mass transport increases three times from $2.0 \times 10^{-3}$ mol/m$^2$·s to $9.0 \times 10^{-3}$ mol/m$^2$·s when considering ammonia concentration gradient. This result is quite different to those in solute ammonia (NH$_3$-N < 5,000 mg/l) wastewater. The reason is that the mass flux for liquid is much lower than gas. The mass transport of gas is about 10$^2$ times that of wastewater. That is to say the acid supply around fibers is relatively in excess under wastewater conditions and the neutralization reaction hardly increases the thickness of the boundary layers. As mentioned above, we could point out that the ammonia concentration, absorbent concentration and its flow rate dominate the resistance of the gas phase and liquid phase. It will be predicted that the flow of liquid on the shell side has great influence on absorption.

Figure 4 shows mass transfer coefficient $K$ and $N$ vs. mixed gas flow velocity. It can be seen that $K$ increases from $1.5 \times 10^{-3}$ m/s to $4.0 \times 10^{-3}$ m/s with gas flow rate at 1~2.5 m/s. As flow velocity is larger, $K$ has little increase. But the mass transport $N$ always has a nearly linear relationship with $V$. This means the majority of ammonia was absorbed under operation conditions. Figure 5 shows the relationship between mixed gas stay time in the module and ammonia concentration outlet, ($C_{\text{inlet}} = 20$ g/m$^3$). The longer the mixed gas stayed in the module, the less the ammonia concentration in the outlet is. If we want to control the ammonia concentration outlet, for example $C_{\text{outlet}} < 1.0$ g/m$^3$, we should choose a stay time longer than 0.7 s. For full utilization of the module, 3 m/s (gas flow velocity) maybe the optimal. Here mixed gas flux is 4.0 m$^3$/h in the module.
Conclusion

The Hollow Fiber Membrane (HFM) contactor has very high elimination (99.9%) under optimal operation conditions. 5.0 Nm$^3$/m$^2$.h gas purification ability can be achieved, as outlet and inlet ammonia concentration are <0.02 g/Nm$^3$ and 20.0 g/Nm$^3$ respectively and gas stay-time in the Contactor is only 0.04 s when acid supply around the membrane fibers is sufficient. Ammonia was stabilized by the (NH$_4$)$_2$SO$_4$ form in this study. The heat effect is not described here. In practical application, heat effect is also an important factor with influence on mass transfer, module life, etc. Industrial tests indicated that HFM contactor technology could be used to purify mixed gas containing ammonia and replace conventional soft-water washing and absorbing techniques.

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References