ISSN 1001—0742
Journal of Environmental Sciences Vol. 18, No. 6, pp. 1176—1181, 2006 CN 11—2629/X

Article ID: 1001-0742(2006)06-1176-06 **CLC number:** X511; X174 **Document code:** A

Regenerable adsorbent for removing ammonia evolved from anaerobic reaction of animal urine

CHOU Liang-hsing[1], TSAI Ru-in[2], CHANG Jen-ray[2,*], LEE Maw-tien[3,*]

(1. Department of Civil and Water Resource Engineering, "National" Chiayi University, Chia-Yi, Taiwan, China; 2. Department of Chemical Engineering, "National" Chung Cheng University, Chia-Yi, Taiwan, China; 3. Department of Applied Chemistry, "National" Chiayi University, Chia-Yi, Taiwan, China. E-mail: mtlee@mail.ncyu.edu.tw)

Abstract: The waste gas evolved from biodegradation of animal urine contains ammonia causing environmental concerns. A new and effective method for removing ammonia from such waste gas using reactive adsorption is presented. In the process, activated carbon impregnated with H_2SO_4(H_2SO_4/C) is employed. Ammonia in the waste gas reacts with H_2SO_4 on the adsorbent instantaneously and completely to form $(NH_4)_2SO_4$. The H_2SO_4/C adsorbent is high in NH_3 adsorption capacity and regenerable. The NH_3 removal capacity of this regenerable adsorbent is more than 30 times that of the adsorbents used normally in the industry. The spent H_2SO_4/C is regenerated by flowing low-pressure steam through the adsorbent bed to remove the $(NH_4)_2SO_4$ from the adsorbent. The regeneration by-product is concentrated $(NH_4)_2SO_4$ solution, which is a perfect liquid fertilizer for local use. Re-soaking the activated carbon with H_2SO_4 solution rejuvenates the activity of the adsorbent. Thus the H_2SO_4/C can be reused repeatedly. In the mechanism of this reactive adsorption process, trace of H_2O in the waste gas is a required, which lends itself to treating ammonia gas saturated with moisture from biodegradation of animal urine.

Keyword: ammonia removal; regenerable adsorbent; reactive adsorption; biodegradation of animal urine; activated carbon

Introduction

Disposal of livestock wastes are of great environmental concern. Discharging large quantities of liquid manure to rivers results in serious water pollution of the rivers. In addition, the intense foul odor is intolerable. Ammonia is the culprit for the odors. As a result, the treatment of pig wastewater has been the subject of many studies. Separation of concentrated and diluted pig wastewater for further treatment were discussed by Gorecki *et al.* (1993) and Yang *et al.* (1993). Anaerobic treatment was the most popular method and discussed by Yang and Kuroshima (1995), Hill (1982, 1985), Floyd and Hawkes (1986), Yamamoto (1992) and Batstone *et al.* (1997).

Another frequently used process for swine wastewater treatment is an aerobic process, which is used by Jutear (2004) to treat high-strength wastewater. There are other methods: Thorneby *et al.* (1999) used reverse osmosis to treat liquid effluent from dairy cattle and pig. Kim *et al.* (2004) applied integrated real-time control strategy to remove nitrogen in swine wastewater treatment.

In Taiwan, most of the swine wastewater is treated using a three-stage process, consisting of: solid separation, anaerobic reaction and aerobic reaction processes. Foul smelling ammonia is evolved from the anaerobic process. Therefore it is important and urgent to control the ammonia emission to improve the air quality in Taiwan.

To remove ammonia, the wastewater can be treated by stripping with steam or air. However, it is difficult and costly to remove the ammonia to levels below the specification of 10 ppm. In addition, the small quantity of ammonia can escape to the air causing environmental concerns. The other method is aerobic treatment. It requires a large wastewater treating facility, which a typical pig farm cannot afford. Clearly, there is a need to develop an inexpensive and simple method to remove ammonia from wastewater in Taiwan.

In production of ammonium sulfate, ammonia is scrubbed with sulfuric acid. In addition, wet scrubbing has been used to remove ammonia in biological wastewater-treatment process (Cooper and Alley, 1990). Wet scrubbing is effective but suffers from the problems of scaling inside the tower, equipment plugging, and corrosion (Cavaseno 1980). Furthermore, it is costly to dispose the resulting dilute scrubbed solution.

Instead of wet scrubbing, a fixed bed of zeolite or γ-Al_2O_3 can be employed to adsorb and remove NH_3 from the gas stream. However, in the process, the NH_4OH reacts gradually with the adsorbent to destroy its structure, resulting in increased pressure drop, which makes the operation itself impossible. Moreover, the great quantity of used adsorbent has to be disposed off by use of costly landfill.

Recently, Hudson *et al.* (1974), Tsutsui and Tanada (1987), Brown (1989), Amos Turk *et al.* (1989), and Nevskaia *et al.* (1999) showed that the adsorption properties of the activated carbon can be improved by impregnating it with acid or base solution. Such modified product is called Impregnated Activated Carbon (IAC). Yan (1997) showed that the adsorption efficiency and capacity of IAC are higher than that of the activated carbon itself. Previously, we

* Corresponding author

have disclosed a new method to remove HCl from the acidic gas stream by reactive absorption, using NaOH IAC (NaOH/C) (Lee *et al.*, 2003). The experimental results indicated that the NaOH/C has a much higher HCl removal capacity than alumina, generally used in the refinery to remove HCl from refinery gas streams. Moreover, we also showed that NaOH/C is regenerable without generating waste for disposal.

It is thought that a similar principle can be applied to prepare a regenerable adsorbent, H_2SO_4/C to remove NH_3 from waste gases. It is important to note that the NH_3 containing gas from biodegradation of animal urine is saturated with moisture, which is not amenable to treatment using conventional solid adsorbents. In this study, passing an air stream through a reservoir filled with NH_3 simulated evolution of waste gas from biodegradation of animal urine. The effluent was saturated with moisture and contained the desired level of NH_3. This effluent was sent to an adsorption reactor for the test. The details of the preparation procedure, adsorbent testing and regeneration procedure, and efficacy of the adsorbent are described in this paper.

1 Experimental

1.1 Materials and H_2SO_4/C adsorbents preparation

The carbon-supported acidic adsorbent, H_2SO_4/C was prepared by impregnating the activated carbon with sulfuric acid solution. The same procedure was used to re-impregnate the regenerated activated carbon right in the reactor for reuse in the next adsorption cycle. The activated carbon (GAC 830) was purchased from Norit Americas Inc., Atlanta, Georgia USA and the properties were as follows: particle size, 2 to 5 mm; surface area, 1050 m^2/g; pore volume, 0.85 ml/g; iodine No., 75 mg/g; minimum and apparent density, 0.54 g/ml. In preparing the H_2SO_4/C, the activated carbon was packed in an adsorption reactor to form a fixed bed and dried at 120℃ by passing through air to remove physically adsorbed water. The dried activated carbon was brought into contact with an equal volume of sulfuric acid solution. Upon soaking for 30 min, the reactor was purged with N_2 for 30 min. The resulting material was noted as H_2SO_4/C. In order to obtain H_2SO_4/C with various levels of H_2SO_4 loadings, the concentration of H_2SO_4 solution was varied from 0 to 16 mol/L. For simplification, the H_2SO_4/C prepared from x mol/L H_2SO_4 was noted as HIAC(x). The actual sulfuric acid concentration on the H_2SO_4/C was determined by titration, employing 6 mg/L NaOH aqueous solution as the titrant.

1.2 Performance test of the H_2SO_4 /C (HIAC) adsorbents

The HIACs were tested in a continuous up flow fixed-bed reactor. The reactor was a polyvinyl ethylene tube with an inside diameter of 2.5 cm and length of 50 cm. In order to demonstrate feasibility of *in-situ* regeneration and rejuvenation of the adsorbent for multiple cycles of operation, HIAC was prepared in the reactor according to the following procedure. For impregnation, sulfuric acid solution of the desired concentration was poured into the reactor packed with 50 g of pre-dried activated carbon for 30 min soaking. The H_2SO_4 impregnated carbon was dried by passing N_2 through the bed for 30 min. The test gas stream was prepared by passing 150 ml/min of dry air through a reservoir filled with NH_3 aqueous solution to pick up NH_3 and moisture. A mass flow controller controlled the total gas flow rate and the NH_3 concentration in the gas stream was controlled by the flow rate of carrier gas as shown in Fig.1. During the test, NH_4OH was continuously added to the reservoir to maintain the pH level at 11.5 using a pH controller. By keeping the pH level of the reservoir constant, the NH_3 concentration in the carrier gas was kept constant. The final NH_3 concentration of 70 μg NH_3/ml air was achieved by breeding in the necessary amount of

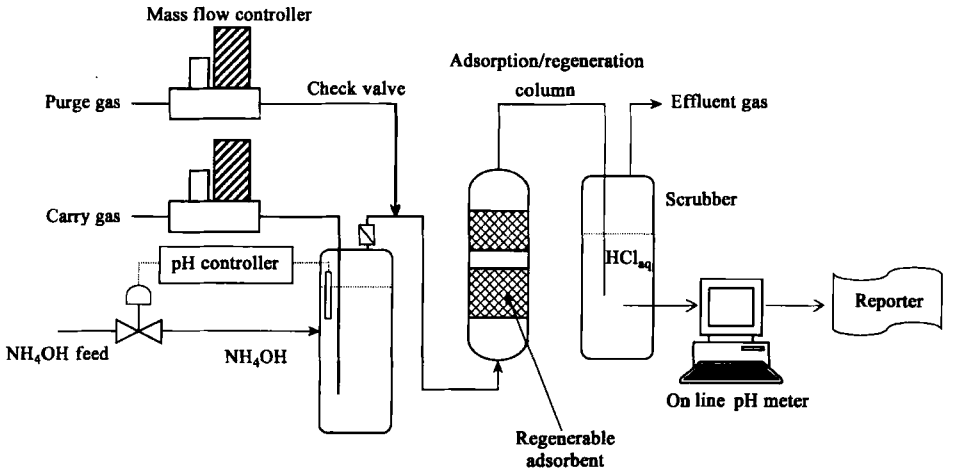

Fig.1 Schematic diagram of the H_2SO_4/C regenerable adsorbent performance tests