



Synthesis of $\text{Fe}(\text{NO}_3)_3$ and H_3PO_4 Combined Pelletized Activated Carbon Composites for Removal of Ultrafine Pollutant Gases (NH_3 , CO_2 and H_2S)

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Received: 16 July 2018;

Accepted: 15 March 2019;

Published online: 29 April 2019;

AJC-19382

In the present study, the potential of pelletized activated carbon (PAC) inoculated with $\text{Fe}(\text{NO}_3)_3$ and H_3PO_4 as packing material for NH_3 , CO_2 and H_2S removal from mixed waste gases was evaluated. Broad tests were conducted to determine the factors affecting the removal of high concentrations of NH_3 . The removal characteristics, removal efficiency, and removal capacity of the system were evaluated. The results of bed depth service time experiment suggested that the removal of NH_3 , CO_2 and H_2S results from physical adsorption of the gases by pelletized activated carbon. The vigorous steady state of physical adsorption lasted for approximately 4 h. After the system achieved equilibrium, the pelletized activated carbon bed exhibited high adaptation to shock loading, elevated temperatures, and high flow rates. The results also demonstrated that the removal of NH_3 was not affected by the presence of H_2S . Gas retention time was a crucial factor affecting system performance. A retention time of $\geq 65\text{s}$ was required to obtain NH_3 removal efficiencies of $\geq 15\%$. The acute loading of NH_3 for system was $4.2\text{ gN/m}^3/\text{h}$ and the maximal loading was $16.2\text{ gN/m}^3/\text{h}$. The results of this study can be used as a guide for the design and operation of industrial-scale systems in the future.

Keywords: $\text{Fe}(\text{NO}_3)_3$ and H_3PO_4 , Pelletized activated carbon, Hydrogen sulfide, Ammonia, Carbon dioxide.

INTRODUCTION

In Korea, the greening of walls of buildings owing to the growth of climbing vegetation is commonly observed. Greening may occur naturally or may result from the deliberate planting of climbers for esthetics reasons, achieving temperature modification or insulation, and promoting ecological values. A new area of research is currently examining the protective role of pelletized activated carbon (PAC) composites against airborne dust and pollutants and interactions between PAC and the pollutants. The present study focuses on the role of climbing vegetation on walls in removal of ultrafine dust [1]. The topic of this study is highly relevant to present-day air pollution because airborne particulate matter (PM) has been associated with the degeneration of wall surfaces, respiratory ailments, and death in extreme cases. In addition, a majority of fine (< 2.5 micron in diameter) and ultrafine (< 1 micron in diameter) particulate matter arise from anthropogenic activities; for example, vehicular pollution and gaseous industrial emission of hydrogen

sulfide (H_2S), carbon dioxide (CO_2) and ammonia (NH_3) are the major contributors of particulate matter [2-4]. The result of this study indicate that pelletized activated carbon composites combined with $\text{Fe}(\text{NO}_3)_3$ and H_3PO_4 can act as a "particle sink" because dust adheres to the PAC composites; thus, PAC mitigates the effect of air pollution on people and the built environment.

Moreover, H_2S , CO_2 and NH_3 are emitted concurrently into the atmosphere from various facilities, including carcass-processing plants, sewage treatment plants, composting works, livestock farms and wastewater treatment plants [5-7]. In addition to being toxic, these emissions create a nuisance in factories. The traditional methods of treating waste gas include carbon adsorption, wet scrubbing, thermal incineration and catalytic incineration [8]. However, these methods are associated with prohibitive costs and secondary waste streams [9]. In response to high levels of air pollution, regulatory authorities are mandating measures for highly stringent control of gaseous pollutants (particularly for malodorous compounds). Consequently, the

demand for cost-efficient air pollution control technology is expected to increase. Currently, pelletized activated carbon is regarded as the most effective available control technology for treating diluted pollutants or odorous compounds because it is more economical than other technologies and generates minimal secondary waste streams [10-12]. Pelletized activated carbon has been considered among the most promising materials for treating waste gases using air-phase reactors [13,14]. The reactor consists of a simple packed-bed column containing microbial populations and solid supports.

The microorganisms form a biolayer on the surface of packing material. In a PAC, water may not be applied or may be applied only intermittently. Moreover, water layer is extremely thin and is often considered to create a practically negligible barrier to polluted air or water. Therefore, when contaminated air or water passes through the material, the pollutants are transferred to the biolayer, where they are biodegraded by the resident microbes. Previous studies have shown that various inoculated bacteria [15,16] and packing material [17] have been used for the removal of gaseous pollutants. Several reports have evaluated the use of air-phase reactors for the removal of H₂S and NH₃ [7,14,18,19] which are emitted during processes such as leather manufacturing, wastewater treatment, asphalt production, and pulping.

Screening methods for the selection of the appropriate type of PAC as well as selection guidelines for the packing material have been previously established [13,20,21]. The present study only focused on evaluating removal efficiency, removal capacity, removal kinetics and reaction mechanisms. The treatment of H₂S with PAC exhibited a removal efficiency of 27 % [22-25] and 15 % of NH₃ emissions were eliminated using different types of reactors [16,26-28]. However, only a few studies on PAC have focused on or presented data on the risks of aerosol emission, pressure drop or treatment cost. The aerosolization of pathogenic or non-pathogenic microbes is an unavoidable consequence of the use of air-phase reactors. The determination of aerosol concentrations is essential for assessing the safety of reactor use. Ottengraf and Konings [29] evaluated discharged aerosols from six full-scale biofilters located in the Netherlands. According to their inferences, the mean aerosol concentration in the outlet gas discharged from the reactors was marginally higher than that encountered in the open air but of the same order of magnitude as that encountered in indoor air. Furthermore, they concluded that PAC considerably reduced the concentration of particulate matter in a highly contaminated inlet gas [29]. Because partial peat PAC emits considerable quantities of bioaerosols during long-term use of the reactor [30], assessing the environmental risk associated with the new system is imperative. A high pressure drop often results from aging of the packing material (*e.g.*, compost or peat) [31], thus leading to a relatively high energy demand and high operational costs. Each of these parameters becomes crucial when the system is used for field applications. The consideration of cost and economy is indispensable while demonstrating the feasibility and effectiveness of a new system. Generally, capital costs include the costs of system equipment, medium, and piping. Operating costs arise from energy and water consumption as well as disposal, maintenance and medium

replacement. However, assessing highly specific capital and operating costs is difficult because of variability in waste gases, performance requirements, and system design [32]. In general, the capital cost for small-scale designs (100 m³) have been estimated at US \$ 1000-3500 per m³ of filter bed. In increase in bioreactor volume can reduce the cost by approximately one-third [33]. Operating costs vary among systems; however, in general, the annual operating cost has been reported to range from US \$ 0.1-3 per 1000 m³ of waste gas treated [34]. Furthermore, metabolite analysis and surveillance of the microbial population of the biofilter can improve the removal efficiency of a biosystem under different conditions. Therefore, in this study, several operational characteristics of PAC biofilter during the simultaneous treatment of H₂S and NH₃ were examined; these included the acidification phenomenon, safety considerations and economic evaluation. Direct evidence showed that the microbial population in this system performed satisfactorily during the operational period.

EXPERIMENTAL

Medium preparation: The original pure culture strains of a heterotrophic ammonia oxidizer, *A. oxydans* CH8, and a heterotrophic sulfur oxidizer, *P. putida* CH11, were isolated from swine wastewater [6,16]. These bacteria were purified by repeatedly transferring the cells to fresh medium. Both the stock cultures were enriched in nutrient broth at 30 °C. The nutrient broth contained yeast extract (5 g/L), tryptone (10 g/L) and dextrose (2 g/L). In our continuous-treatment experiments, the inflow medium was used and stored in the nutrient tank. The inflow medium contained glucose (10 g/L), KH₂PO₄ (4.08 g/L), K₂HPO₄ (5.22 g/L), NH₄Cl (0.4 g/L), MgCl₂·6H₂O (0.2 g/L), and Fe(III) citrate (0.01 g/L). The final pH level of culture medium was adjusted to pH 7 using 2 N NaOH or HCl. The buffer capacity (*i.e.*, the ratio of increment of strong base or strong acid to the change in pH) in the inflow medium was 0.033 (M/pH).

Immobilization procedure: Pelletized activated carbon obtained from Chong Tay Corporation Ltd., Korea, was used as the packing material for the biotrickling filter. The main characteristics of PAC were as follows: bulking density: 0.48 g/cm³, specific surface area (SSA): 1250 m²/g and pH: 9. Cultures of *Arthrobacter oxydans* CH8 or *Pseudomonas putida* CH11 were grown in 1000 mL of nutrient broth and harvested by centrifugation (8000 × g for 10 min). The precipitates were collected and mixed with 7 L of nutrient broth in a 10 L PVC tank for enriched growth. Approximately 3 g of PAC were separately mixed with the enrichment solution to obtain a film of immobilized cells. During the cultivation period, broth was replenished every 3 days until the cell numbers of *A. oxydans* CH8 and *P. putida* CH11 reached approximately 10¹⁰ CFU/g dry PAC. After 2 days, the cell-laden PAC medium in the tank was transferred onto the biotrickling filter.

Gas removal for continuous operation: To investigate the adsorption capacity of PAC toward NH₃, three glass columns (diameter: 12 cm; working length: 7 cm) were connected in series. The columns were packed with only PAC (without microbes) for the bed depth service time experiment. Ammonia (NH₃) at a concentration of 110 ppm was continuously supplied to the glass columns at a flow rate of 5 mL/h. The outlet NH₃

concentrations in each column were measured separately at 1 h intervals. The desired concentration of NH_3 at the breakthrough was defined as 24 ppm (*i.e.*, $C_c/C_0 = 0.4$, C_c and C_0 were the desired and inlet NH_3 concentrations, respectively). The experimental results could serve as background values for continuous operation of PAC. A schematic of pilot-scale PAC reactor is shown in Fig. 1. Two glass columns (diameter: 12 cm; working height: 40 cm) were connected in series. The columns were packed with cell-laden PAC supported by a perforated sieve plate at the bottom of the column to allow drainage of the circulating liquid. The initial packed volume, dry weight of PAC and number of cells in the biotrickling filter were 9.05 mL, 4.34 g and 3.8×10^{10} CFU/g dry PAC, respectively. The column walls contained four sampling ports, 25 cm apart, for sampling or measuring the concentrations of NH_3 and H_2S during the experiments. The gas flow through the reactor was controlled using a flow meter and valve. The $\text{NH}_3(\text{g})$ and $\text{H}_2\text{S}(\text{g})$ were supplied by separate gas cylinders. The two gases were first diluted with compressed air, which passed through an air filter (pore size 0.2 μm , LIDA 3000-06, made in USA). The diluted gases then flowed downward from the top to the bottom through the biotrickling filter. A peristaltic pump was used to intermittently recirculate the inflow medium (see medium preparation) from the nutrient tank at a flow rate of 10 mL/min for 6 min once in 4 h to maintain an optimal moisture level on the biotrickling filter and supply nutrients to the attached cells. The peristaltic pump was connected to a spray nozzle to uniformly spray the medium on the surface of the filter bed. The directions of the medium and influent gas were opposite to each other. A glucose solution (10 g/L) was added once every 2 weeks. During the 140 days treatment periods, different concentrations of NH_3 (80-120 ppm) under constant inlet H_2S loading (6.25 $\text{gS}/\text{m}^3/\text{h}$) were supplied to PAC biotrickling filter at various flow rates (180-1440 L/h) to evaluate the system performance.

Experimental design: Response surface methodology (RSM) as described first by Box *et al.* [35], is an effective experimental design to determine the optimal operation conditions for multivariable systems. The combined effect of inlet concentration and gas flow rate on NH_3 removal was investigated through RSM. In the present work, a central composite design for two variables was used to determine the response pattern. The experiment had a full-factorial design, comprising a two-factor two-level pattern with 11 design points; the design included nine combinations with three replications of the center points. Multiple regression analysis was performed to obtain the coefficients, and an equation was used to predict the response using the STATISTICA program Version 5.0 (StatSoft Inc., Tulsa, OK).

Analytical methods: A D8 Advance X-ray diffraction (XRD) analysis instrument (Bruker AXS, Germany) with $\text{CuK}\alpha$ radiation (40 kV, 40 mA) over a 2θ range of 10° - 80° was used to investigate the mineralogy of the PAC samples. Scanning electron microscopy (SEM, Quanta 200, FEI Company, USA) coupled with energy-dispersive X-ray spectroscopy (EDS, Quanta 200, FEI Company, American). The inlet NH_3 gas concentrations (2.5-200 ppm) in the reactor were periodically measured using gas detector tubes (Model 3LA, Kitagawa, Japan). The outlet concentrations (0.01-0.2 ppm) were continuously measured using a Single Point Monitor (MDA Scientific, USA) or (Model 3L, Kitagawa, Japan). In all continuous experiments, the NH_3 concentrations were recorded as variations in the NH_3 concentration within $\pm 5\%$ in 2 h. In total, 12 data points were recorded and the mean value was considered to be the NH_3 outlet concentration. To determine the moisture content in PAC, approximately 5 g was withdrawn, weighed and dried for 24 h at $103 \pm 0.5^\circ\text{C}$. To measure the pH value, 0.5 g of PAC was withdrawn through a suitable sampling port and mixed with 5 mL of distilled water. The mixture was vortexed for 3 min

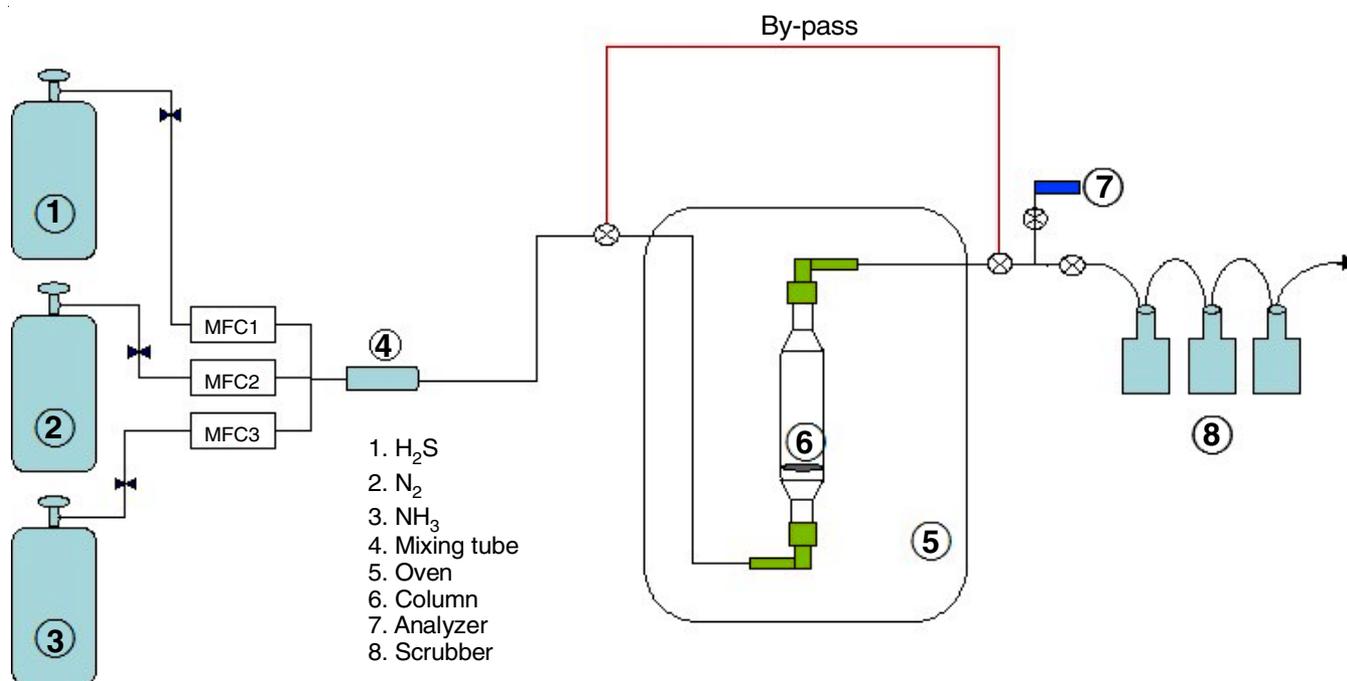


Fig. 1. Column type adsorption capacity measurement device configuration

and the pH value was then determined using a pH meter (Model SP-2200, Suntex, USA). To understand the changes in the pH of leachate, 20 mL of circulating liquid was withdrawn from the nutrient tank at regular intervals to measure the pH values. For microbial analyses, 0.5 g samples of PAC were separately drawn from sampling ports at different depths and mixed with 5 mL of sterile water. The mixtures were vortexed for 3 min, and the cell numbers were enumerated using traditional plate-counting methods. In this study, Luria-Bertani (LB) medium for heterotrophic microbial cultivation, Hagedorn and Holt [36] selective medium were used for *A. oxydans* spp. and the cetrimide-selective medium for *P. putida* CH11 were used [37]. The inoculated plates incubated for 2 days at 26 °C.

RESULTS AND DISCUSSION

XRD analysis: In the XRD spectrum of PAC, A6-HP exhibited typical patterns at 22.5°, 32.5°, 42.5°, 47°, 50°, 52.5° and 58.9° (Fig. 2), while A6-FN exhibited typical patterns at only 25°. The crystallites observed on the PAC surface indicated the crystalline phase of carbon (Fig. 3); this finding is contrary to those in virgin activated carbon [38]. In this study, carbon atoms in PAC formed a stable lamellar graphite crystal structure. The structure was associated with a large lamellar gap; consequently, a high SSA was obtained. However, PAC is a graphite based amorphous carbon material. This is consistent with the studies of PAC [39,40].

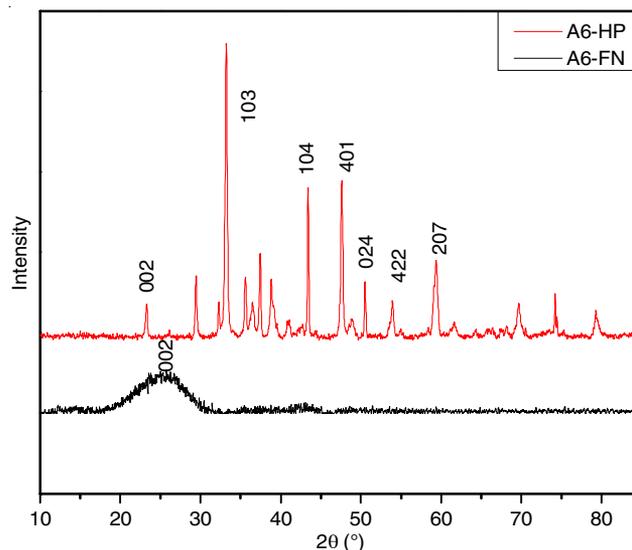


Fig. 2. XRD pattern of A6-HP and A6-FN samples

Morphological analysis: Figs. 3 and 4 show the SEM and EDS analyses of PAC, respectively. At a high resolution, an uneven and rough PAC surface was observed with abundant protuberances and many laminated structures, which favoured the diffusion of H_3PO_4 to the PAC surface. The corresponding EDS spectrum of the focus area in the SEM image was obtained

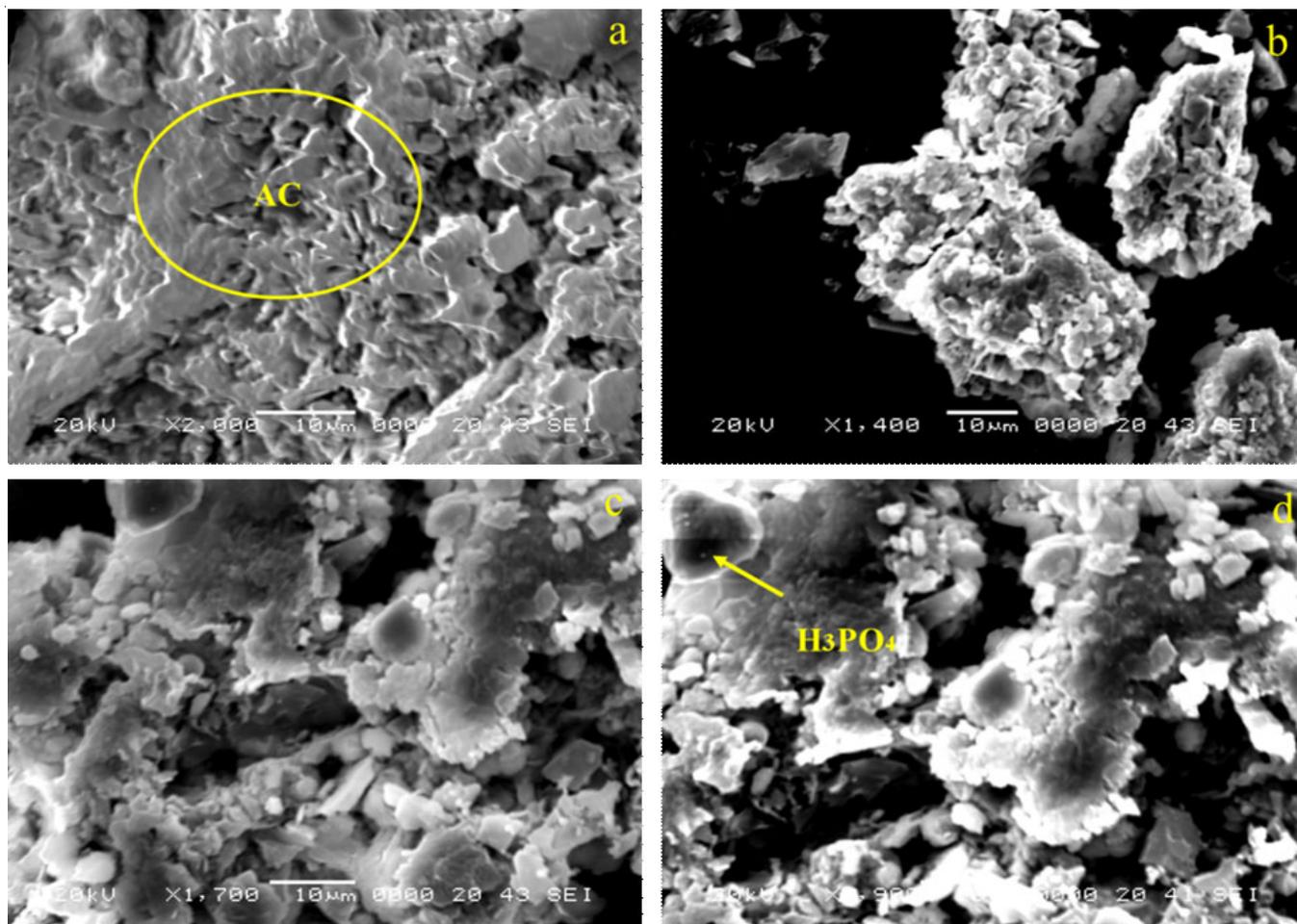


Fig. 3. SEM image of A6-FN (a,b) and A6-HP (c,d) samples

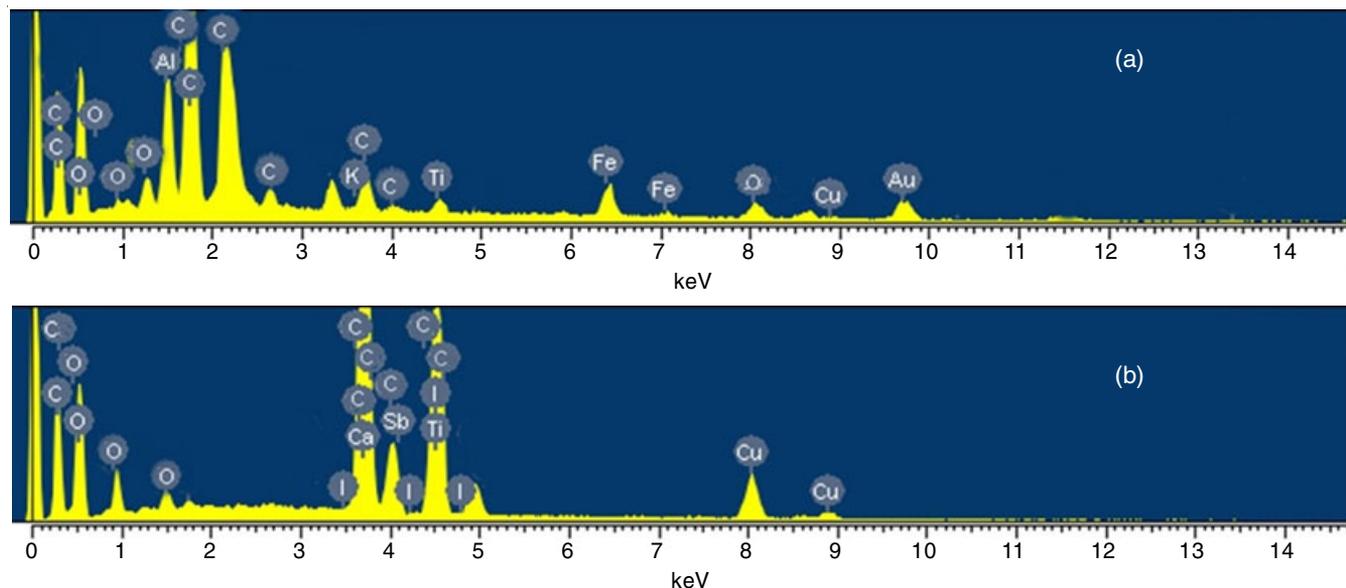


Fig. 4. EDX results (a) EDS of Fe(NO₃)₃ treated AC and (b) EDS of H₃PO₄ treated AC

to determine the elemental composition (Fig. 4). The concentrations of C, O, Al, Cu, Fe and Ca were 86.40, 12.89, 0.08, 0.31 and 0.07 %, respectively. In case of A6-HP, the concentrations of C, O, I, Cu, Sb and Ca were 84.40, 14.89, 0.08, 0.31 and 0.07 %, respectively. The concentrations of Cu, Al, Ca, Sb, and O in PAC facilitate the prediction of the properties of PAC required for pelletized production [41]. By contrast, the surface properties could serve as the main adsorption sites for NH₃ removal. This was consistent with the results obtained for furfural removal using PAC [42].

Adsorption of NH₃ by PAC: Before NH₃ oxidation by the microorganisms in biofilm, the physical adsorption of NH₃ by PAC begins as soon as waste gases are introduced. The results of adsorption are shown in Fig. 5. The adsorption process is described by the following equation [43]:

$$t = \left(\frac{N_0}{C_0 V} \right) X - \frac{1}{KC_0} \ln \left(\frac{C_0}{C_c} - 1 \right) \quad (1)$$

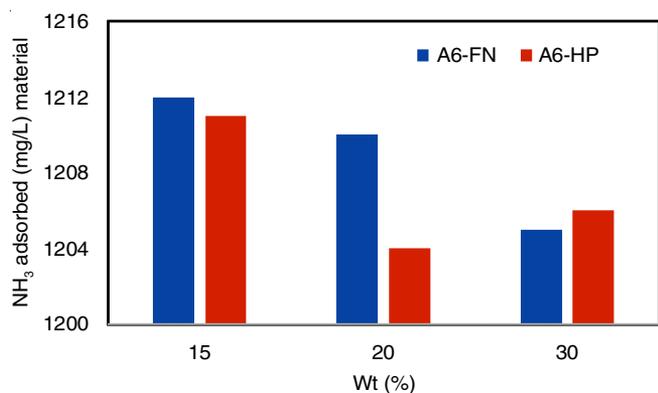


Fig. 5. NH₃ absorption measurement result for A6-FN and A6-HP sample

In eqn 1, C_0 = inlet NH₃ concentration (mg/L); C_c = desired NH₃ concentration at breakthrough (mg/L); V = hydraulic loading (cm/h); t = service time (h); X = bed depth (cm); N_0 = adsorptive capacity (mg/L) and K = adsorption rate constant (L/mg/h).

The equation constants were obtained by using the regression method and the values of slope and intercept were 0.83 and 3.09, respectively. Accordingly, adsorptive capacity (N_0) was 280.9 mg/L and adsorption rate constant (K) was 1.71 L/mg/h. The adsorptive capacity, expressed in terms of dry weight of PAC, was approximately 0.6 mgN/g dry PAC. The NH₃ adsorption capacity of pure PAC can provide a reference value for the removal capacity of cell-laden PAC. In this study, PAC used was physically saturated on the 10th day in the continuous experiment under actual operating conditions.

High concentrations of NH₃ removal from mixed H₂S in continuous operation: The removal efficiency of NH₃ profile in the PAC biotrickling filter during the 140 days operation is shown in Fig. 6. In this study, NH₃ concentrations (80-120 ppm) and gas flow rates (180-1440 mL/h) varied, while inlet H₂S loading was fixed at 6.25 gS/m³/h; a removal efficiency of 27 % was sustained. We evaluated the performance of the system for NH₃ removal under the aforementioned conditions. The theoretical saturation time for NH₃ adsorption was approximately 2 days when the adsorption equation was used for estimation. However, the adsorption period decreased owing to concurrent presence and competitive adsorption of H₂S. Hence, the physical adsorption of PAC was responsible for 100 % NH₃ removal in the first 7 days as shown in Fig. 6. After 7 days, the NH₃ removal efficiency gradually decreased and the removal efficiency was only 15 % at the outlet of the filter bed on the 15th day. Afterward, the removal efficiency gradually increased, and the total removal efficiency of PAC trickling filter was as high as 98 % on the 2nd day. Thus, a two-days acclimation period or lag phase was required for biological NH₃ removal. The initial NH₃ load (1.5 gN/m³/h) was increased 4-fold (6 gN/m³/h) and 12-fold (18 gN/m³/h) on days 5 and 118, respectively, to test the adaptability of PAC biotrickling filter to shock loading. The high removal efficiency (> 98 %) of NH₃ immediately reduced to 87 % and 48 % under the 4-fold and 12-fold shock loads. The unit for microbial enumeration as CFU/g dry PAC.

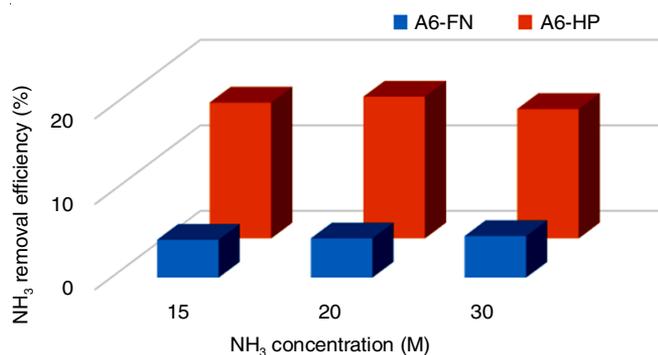


Fig. 6. NH₃ gas removal efficiency of A6-FN and A6-HP sample

However, when the original inlet NH₃ level (1.5 gN/m³/h) was restored, a high removal efficiency was obtained within 2 or 3 days. These results indicated that the system adjusted satisfactorily to shock loading and continued to operate effectively despite considerable fluctuations in NH₃ loading; fluctuations are likely to occur during actual industrial operations. Over the 4 months study, an average NH₃ removal of 96 % was obtained. Under similar operating conditions, the efficiencies of other systems, such as compost bed, peat bed, wood-bark bed and PAC biofilter) were lower than those of PAC biotrickling filter inoculated with *A. oxydans* CH8 and *P. putida* CH11. Removal ability of the other systems were 85-93 % [43]. Although the removal efficiency of the PAC biotrickling filter was slightly lower than that of the immobilized cell biofilter using Ca-alginate as a carrier [44], it exhibited a high removal efficiency during strongly fluctuating NH₃ inputs in the long-term use experiment. These results suggested that PAC trickling filter is more appropriate than Ca-alginate biofilter for field applications. Rapid physical adsorption and effective biooxidation resulted in successful removal of NH₃ by the PAC trickling filter. Simultaneous bioregeneration of carbon was an additional economic advantage of the system.

From the profile of heterotrophic bacterial numbers, we found that initially inoculated cells were about 3.8×10^{10} CFU/g dry PAC. The cell numbers decreased to 3×10^9 CFU/g dry PAC on the third day owing to scrubbing by circulating solution (data not shown). During the 140 days experiment, except for the first several days, the variation in the cell number was 10^9 - 10^{10} CFU/g dry PAC in the samples obtained from different sampling ports. In addition, the profile of cell numbers did not exhibit gradient changes along the length of column; the highest cell numbers were observed in the middle zone of trickling filter (data not shown). Because NH₃ removal by heterotrophic bacteria was considered a detoxification process, high NH₃ concentrations were expected to inhibit microbial activity in the inlet zone of biotrickling filter [45]. Table-1 shows the cell numbers and distribution ratios of the inoculated cells (*A. oxydans* and *P. putida*). The results indicated that the ammonia oxidizer, *A. oxydans* was the dominant microorganism, which accounted for 87.9, 93.1 and 94.2 % of the total microbial community on days 45, 120 and 138, respectively. The sulfur oxidizer, *P. putida* accounted for 12.1, 6.9 and 5.8 %, respectively, on days 45, 120 and 138. Although the distribution ratios of *P. putida* decreased slightly, complete H₂S removal was still achieved during the operational period. The results also

TABLE-1
NH₃ ADSORPTION CAPACITY OF Fe₂O₃
TREATED ACTIVATED CARBON

Sample	Temp. (°C)	NH ₃ adsorption capacity (mg/g)	NH ₃ adsorption capacity (mmol/g)
15 % Fe ₂ O ₃	300	129.582	2.945
	600	237.623	5.401
	700	298.467	6.783
20 % Fe ₂ O ₃	300	107.161	2.436
	600	250.951	5.704
	700	294.596	6.695
50 % Fe ₂ O ₃	300	94.412	2.146
	600	135.850	3.088
	700	203.869	4.633

demonstrated that the inoculated cells of *A. oxydans* sustained high distribution ratios and cell numbers in the bacterial community during fluctuations in loading and temperature on day 2 and day 3, respectively. These findings indicated an additional characteristic of the PAC trickling filter, which renders it advantageous for field application.

Effect of temperature change on removal of NH₃: Temperature is a crucial factor affecting the physical adsorption of NH₃ by PAC and bio-oxidation by microorganisms. To evaluate the system response to temperature variation, NH₃ removal efficiencies with temperature change are shown in Fig. 7. During the entire experimental period, an environmental temperature of 26 ± 2 °C except on days 3-4. The temperature was increased to 45 °C after operation for 4 days and a significant decrease in NH₃ removal efficiency (23 % from 99 % to 76 %) was observed. Considering that the optimum temperature for the growth of *A. oxydans* CH8 was 26 °C [46], the increase in temperature could have resulted in low removal efficiency. To obtain a detailed understanding of the response system to temperature change, the concentrations of NH₃ and H₂S were controlled at 100 ppm and 30 ppm, respectively, at a flow rate of 720 mL/h. The temperature variation experiments were conducted at 15, 45 and 26 °C (Fig. 7). When temperature increased from 15 to 45 °C in 4 days, the removal efficiency decreased from 94 % to 75 %. However, 94 % removal of inlet NH₃ was achieved within 1 day after the environmental temperature was returned to 26 °C. In the meantime, H₂S removal was sustained at 100 % across the operational temperatures. Furthermore, the data indicated that temperature change did not reduce the amount of PAC (Table-1). Therefore, high temperature may reduce

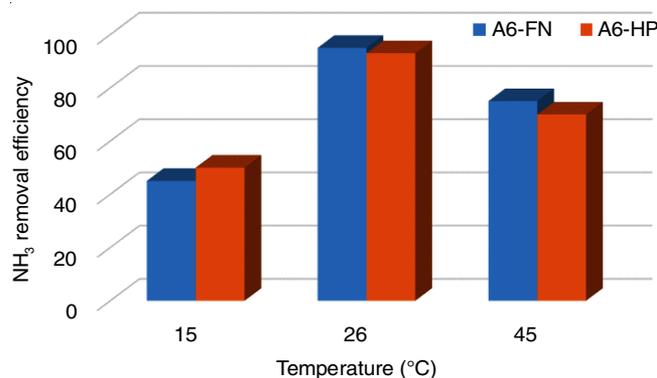


Fig. 7. Removal efficiency of NH₃ with temperature variation for A6-FN and A6-HP

physical adsorption of NH₃ by PAC, thereby reducing removal efficiency.

Effect of H₂S concentration change on NH₃ removal:

According to the results of a previous study, high concentrations of H₂S in Ca-alginate biofilter affected NH₃ removal [47]. To understand the effect of presence of H₂S on NH₃ removal from mixed waste gases in PAC biotrickling filter, the concentrations of H₂S were varied (10-120 ppm) at a constant flow rate of 360 mL/h. The NH₃ inlet was maintained at 100 ppm. Apparently, NH₃ removal was not affected by the presence of H₂S at all tested concentrations in this operating system (data not shown). NH₃ removal efficiency exceeded 96 % under all operating conditions with a deviation within ± 0.5 %. In a previous study, the removal efficiency of NH₃ declined in the Ca-alginate biofilter system because of the presence of acid H₂S [48]. Therefore, these results suggested that PAC can facilitate the pH stabilization of the system and achieve high NH₃ removal efficiency even in the presence of H₂S.

Effect of gas retention time on NH₃ removal: Attached microorganisms can take a longer time to decompose pollutants in a filter than do free-living ones. The delay results in long retention times. Hence, gas retention time is a crucial factor in pollutant removal [49]. When waste gas containing 80 ppm NH₃ was fed into the bioreactor, the removal efficiency decreased with decrease in gas retention time (data not shown). A retention time of 65 s was a critical condition in this study. When retention time was longer than 65 s, NH₃ removal efficiency was higher than 97 %. The removal efficiency decreased considerably if retention time was less than 65 s. For example, a significant reduction in the NH₃ removal efficiency (22 %) was observed when retention time was shortened to 20 s. Therefore, NH₃ removal in the system was dependent on gas retention time. According to Michalis-Menten theory, when the gas retention time is sufficient, the biological reaction rate becomes the rate-determining step (RDS). However, if gas retention time is insufficient, the mass-transfer rate becomes the RDS. Hence, a gas retention time of at least 65 s is necessary for NH₃ removal when the PAC biotrickling filter system is used to remove H₂S and NH₃ gas mixtures.

Comprehensive evaluation of concentration and flow rate for NH₃ removal: The most crucial operating factors affecting NH₃ removal are inlet NH₃ concentrations and gas flow rates. The combined effect of these two factors was evaluated in the present experiments, which involved different inlet concentrations at different flow rates (Table-2). Optimal combinations for NH₃ emission limits were determined. According to the results of experiments, the following equation gives the relative NH₃ removal efficiency, y as a function of inlet concentration, and flow rate was obtained:

$$y = 102.781 - 0.0013x_1 - 0.0061x_2 - 0.00011x_1x_2 \quad (2)$$

where x_1 = NH₃ concentration and x_2 = gas flow rate.

According to the above equation, all the factors exert negative effects. The equation also suggests that x_2 (gas flow rate) is the most crucial factor, with its coefficient effect being the most evident. The contour plot (Fig. 8) explains the behaviour of the system. If > 95 % of NH₃ removal efficiency was achieved at inlet NH₃ concentration of 60 ppm, gas flow rates of < 500 mL/h were necessary. Furthermore, 97 % NH₃ removal was

Sample	Temp. (°C)	NH ₃ adsorption capacity (mg/g)	NH ₃ adsorption capacity (mmol/g)
15 % H ₃ PO ₄	300	125.629	2.855
	600	251.483	5.716
	700	299.273	6.801
20 % H ₃ PO ₄	300	97.739	2.221
	600	203.474	4.624
	700	270.301	6.143
50 % H ₃ PO ₄	300	87.068	1.979
	600	150.383	3.418
	700	192.932	4.385

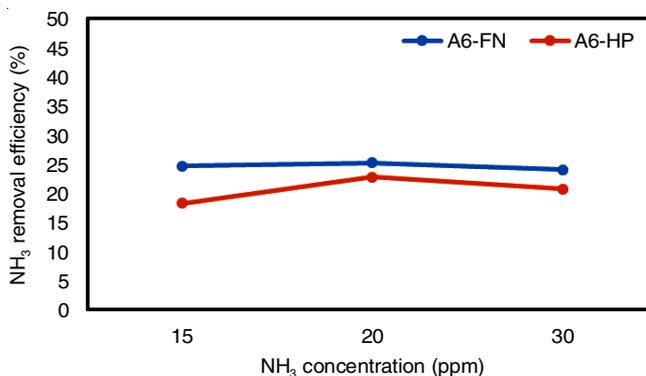


Fig. 8. NH₃ gas removal efficiency of A6-FN and A6-HP sample

obtained when the gas flow rate was < 250 mL/h. Using the contour plot and associated equation, a set of suitable operating combinations can be determined when the system is operated in the field.

Pressure drop: The economic aspects of processes are nearly as crucial as operational efficiency; they must be considered while designing practical PAC reactors. Pressure drop, a common problem in long-term operations, is a crucial parameter that affects operational cost [15]. A high pressure drop increases the energy consumed to maintain satisfactory performance of a reactor. Operational cost increases as a consequence of an increase in energy input. Pressure drop is often caused by the aging of the packing material [50]. Easily biodegradable and compressible packing material, such as compost or peat, exhibits aging. Figs. 9 and 10 depicted the relationship between gas flow rate and pressure drop. In this experiment, the flow

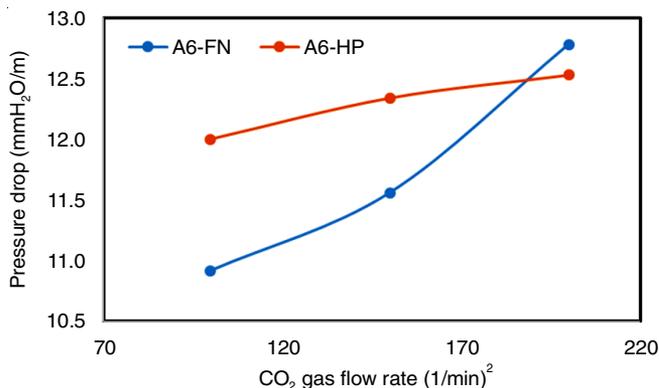


Fig. 9. Measurement of pressure drop through the activated carbon pellet containing in U tube by CO₂ gas

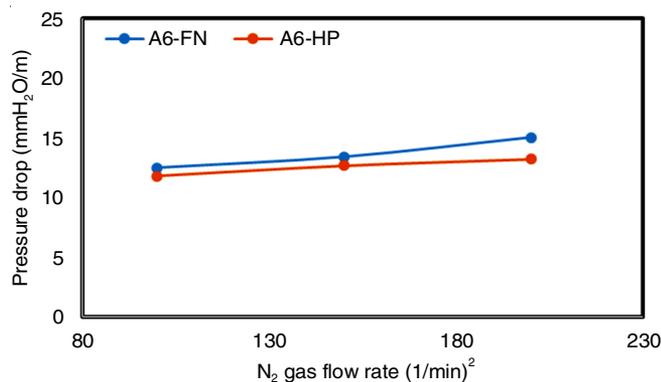


Fig. 10. Measurement of pressure drop through the activated carbone pellet containing U tube by N₂ gas

rate was gradually increased from 180 to 1080 mL/h, and the temperature was maintained at 26°C. When the variation of outlet H₂S/NH₃ concentration was within 5 %, a new flow rate was selected. The results indicated that pressure drop of the biofilter increased with an increase in gas flow rate (data not shown). When the relationship between pressure drop and the square of velocity was drawn, a linear plot passing through all four points was obtained ($R^2 > 0.997$). The pressure drop varied between 8 and 65 mm H₂O/m and corresponded satisfactorily with the operational standard for biofilters (< 300 mm H₂O/m [42]). The pressure drop of an activated carbon biofilter is acceptable and suggests that the system possesses excellent dispersion characteristics [17]. After the system was operated for 2 days, the results of pressure drop were superior to those of other studies that used peat (84 mm H₂O/m), rock wool (78 mm H₂O/m), fuyolite (74 mm H₂O/m) and ceramics (73 mm H₂O/m) as the packing media under similar operational conditions; however, the operational times in the studies with other materials were shorter than that in the present study [9,43]. Apparently, PAC was a satisfactory packing material in terms of pressure drop. The results were consistent with the previous study reported by Malhautier *et al.* [7]. However, if the pressure drop of the pellets reached 250 mm H₂O/m, the bed was unclogged by using a backwashing method to reduce the pressure drop of biofilter.

Conclusion

The results of the present study demonstrated that pelletized activated carbon (PAC) efficiently removed high concentrations of NH₃ gas from mixed waste gases containing H₂S, CO₂ and NH₃. During the 2 days operating period, the system achieved average removal efficiencies of 15 and 27 % for NH₃ and H₂S, respectively, without pH adjustment. This system also exhibited high adaptability to shock loading and temperature variation. The presence of H₂S did not inhibit NH₃ removal. Furthermore, the pH did not decrease or increase significantly in this system. In addition, the low moisture demands and high buffering capacity of the system additional advantages. A set of the operating combinations was also established for field applications of the system. Thus, these results suggested that pelletized activated carbon (PAC) specifically inoculated with *A. oxydans* and *P. putida* has considerable potential for NH₃ and H₂S removal from mixed waste gases.

ACKNOWLEDGEMENTS

This work (Grants No. C0510655) was supported by Business for Cooperative R&D between Industry, Academy, and Research Institute funded Ministry of SMEs and Startups in 2017.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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