Assessment of Ammonia Adsorption on to Polymer Tubing

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Abstract. *The adsorption of ammonia on to different polymer tubing used in pollutant stream conveyance was assessed for possible systematic losses. An experimental design with three replications of 32 trials was completed to investigate the adsorption of ammonia based on: 2 temperatures (26.7 and 37.8 ^{o}C), 2 tubing lengths (15.2 and 45.7 meters), 6 inlet concentrations (2, 5, 10, 15, 25, and 35 parts per million (ppm)), and 2 materials (perfluoroalkoxy polytetraflouroethylene (PFA Teflon) and low density poly ethylene (LDPE)). Analysis of each condition allowed for a predictive equation for each material with variables for length (L), temperature (T), and inlet concentration (C). Ammonia adsorption on Teflon was statistically less than LDPE. Tubing length was not significant in modeling ammonia adsorption onto Teflon, but*

was significant for LDPE. There were significant differences between inlet and outlet concentrations of LDPE at 5 and 15 ppm (α=0.05). Overall, ammonia adsorption to Teflon was nearly 1ppm regardless of the magnitude of inlet concentration. This loss on to the Teflon surface was well within the measurement sensitivity of the ammonia analyzer. Further studies should be conducted to verify these results. Future work should include the effects of other factors such as pressure, relative humidity and gas flow rates through the polymer tubing on adsorption of ammonia on tubing used to covey pollutant streams to ammonia analyzers.

Introduction

Ammonia is known to be a principle precursor to small particulate matter formation, which is detrimental to human health (Singh et al., 2001). In addition, ammonia contributes to acidification of ecosystems when reintroduced through rainfall events (Kangas and Sanna, 2001). Current research does not quantify the amount of ammonia that is lost through adsorption of ammonia on different polymers under field conditions. These field experiments are used to determine the emission of ammonia from various sources. With knowledge of the amount of ammonia that is emitted from a source, the total emission of ammonia may be estimated. An accurate and representative estimation of the amount of ammonia produced from a facility is critical for proper environmental permitting and remediation, as well as for the creation of an emissions inventory. This paper quantifies the adsorption of ammonia onto perfluoroalkoxy (PFA) polytetrafluoroethylene (Teflon) and low density poly ethylene (LDPE) tubing under laboratory conditions that simulate conditions when conducting field experiments.

The chemical structure of ammonia is such that it is very reactive. Although the molecular bond is covalent, the nitrogen-hydrogen bonds have a polar contribution due to relatively strong electronegativity of nitrogen compared to that of hydrogen. This polar contribution, in conjunction with the asymmetrical nature of the molecule, develops a considerable dipole moment (Appl, 1999). This dipole moment, orientated normal to the base, in conjunction with the structure of the nitrogen atom placement atop the apex of the pyramid, makes ammonia a strongly adsorbant material. As ammonia approaches a surface, the dipole moment and nitrogen placement draw it into surface sites. Even though the structure of polymers is such that adsorption sites are relatively rare, ammonia is reactive enough to noticeably adsorb on polymers (Kosmulski, 2001).

Analysis of gas – solid physical adsorption equilibrium is important to design separation and purification processes as well as description of conveyance affects on materials. The equilibrium between the fluid phase and the adsorbent phase may be expressed by adsorption isotherms. An isotherm is defined by the amount of gas adsorbed per unit mass of solid at constant temperatures at varying pressures. The derivation of a scientifically based adsorption isotherm was first achieved by Langmuir in 1918 (Kosmulski, 2001).

The Langmuir adsorption isotherm can be derived from the surface reaction in Equation 1.

$$A + S \leftrightarrow AS \tag{1}$$

where:

A = Adsorbate of interest (Ammonia)

S = Empty surface site of material

AS = Surface site occupied by adsorbate

The equilibrium (binding) constant for the reaction characterized in Equation 1 is represented in Equation 2, where theta is defined as a coverage: the ratio of ammonia-containing surface sites to total sites (Equation 3).

$$K_{ads} = \theta(1-\theta)^{-1}a^{-1}$$ (2)

$$\theta_{AS} = \frac{[AS]}{[AS]+[S]}$$ (3)

$$\theta_S = 1 - \theta_{AS}$$ (4)

Where:

θ = Coverage

a = Activity of the adsorbate in solution

AS= Occupied surface site

S= Empty surface site

The magnitude of adsorption depends on the binding constant (K_{sat}) and the sorption capacity ([AS]+[S]). Polymers typically have low binding constants, reducing the coverage for an adsorbate given the activity of the adsorbate (a). However, ammonia has a relatively high adsorbate activity, increasing the coverage for a given binding constant. These competing factors will determine the magnitude of adsorption.

Several recent studies have attempted to quantify the amount of ammonia present in livestock waste (Sommer et al, 2001; Erisman et al, 2001; Aneja et al, 2001). Sommer et al. (2001) research focused on the volatilization of ammonia from sow manure on grassland. To conduct this research a mobile dynamic chamber was constructed. This chamber utilized approximately 6 meters of Teflon tubing and an air pump to convey the pollutant stream through denuder tubes. Aneja et al. (2001) measured the ammonia emission concentration from anaerobic hog lagoons using a dynamic floatation chamber. Teflon tubing is used to convey the pollutant stream from the chamber to a stainless steel ammonia converter, and then to a nitric oxide analyzer. The Teflon tubing length requirements are not specified and the system response is not described.

Roelle, et al. (1999) and Roelle and Aneja (2002) conducted research to detect nitrogen oxide emissions from agricultural soil. This research utilized a dynamic chamber system and a mobile laboratory up to 10 meters in distance from the chamber. Teflon tubing was used to span the required distance from area source to mobile laboratory. The chamber was also lined with 5 millimeters of fluorinated ethylene propylene (FEP) Teflon. None of the previously mentioned studies specifically addresses the potential loss of ammonia through adsorption, whether in steady state conditions or in start-up.

The overall objective of this study was to model ammonia adsorption and desorption through Teflon and LDPE tubing. By experimenting with different inlet concentrations (at the inlet of the tubing being testes), tubing types, temperatures and lengths, a model was created that predicted the amount of ammonia that may be adsorbed to tubing under these conditions. With the ability to predict ammonia losses, tests that are run using Teflon and LDPE tubing can be modified to represent these adsorption losses after the tests have already been performed, or as a factor to use while the experiment is being run. To conduct these experiments following objectives were realized:

1. Create a laboratory setup that will allow for different physical parameters to be varied.
2. Create a dilution system to produce varying ammonia concentrations.
3. Develop an automated program to carry out the necessary experiments.
4. Determine ammonia adsorption as affected by different temperatures, ammonia concentrations, tubing lengths, and tubing materials.

Methods and Materials

Ammonia concentration at the inlet and outlet of Teflon and LDPE tubing was measured using a chemiluminescence analyzer (Thermo Environmental Inc., Franklin, Ma.). A LabVIEW (National Instruments Ver. 5.1.1) program was designed to regulate the flow and concentration of ammonia by using two programmable mass flow controllers (MFCs) to dilute a certified ammonia cylinder concentration. The correct concentration was then conveyed through the corresponding tubing length in each experiment. Both tubing materials had 0.32-cm inside diameters, so the inside surface area of each treatment was equal. The LabVIEW program was used to control the adsorption experiments and calibrate the analyzer. The program allowed for the concentration to be set, but the times used to change gas flows were constant for these experiments.

Three sequences were used: warm up, adsorption, and dilution (desorpion). First, 100% of the flow at 2 LPM was zero grade air. This zero air allowed the analyzer to stabilize and gave a reference zero concentration for the treatment. In tests, a system warm up and stabilization time of 10 minutes was sufficient to let the system warm up: there were no detectable temporal concentration changes. After 10 minutes, the appropriate ammonia and air mixture was formed. The mixing ratio of ammonia and zero air was set by the user selection of concentration in the trial. This ratio was maintained for an additional 60 minutes. After 60 minutes, the flow returned to 100% zero grade air to test for desorption. This desorption sequence lasted for 20 minutes, giving any residual ammonia in the system (tubing, flow controllers, etc.) sufficient time to be removed from the system (desorption). After 90 minutes, the tubing in trial was removed and the calibration system was connected and the same concentration was drawn through the machine. The resultant concentration was considered to be the inlet concentration (C_{in}) to the tubing in same trial. The difference (C_{Diff}) between the outlet concentration and the inlet concentration was used to determine adsorption of ammonia on to each type of tubing being tested. After the trial was completed, the appropriate physical factors (length, temperature, program concentration) were modified for the next trial. The software was reset, and the next experiment was started. As an illustration of this experiment, Figure 1 details the output of one of the experiments. In this trial the treatments are: Teflon, 37.8 $^{\circ}$ C, 45.7 meters, and 15 ppm ideal concentration. For this trial the outlet concentration averaged 13.8 ppm while the inlet concentration was 14.63 ppm. The difference, or amount of ammonia adsorbed from the tubing, was 0.83 ppm (5.6% less than the inlet concentration).
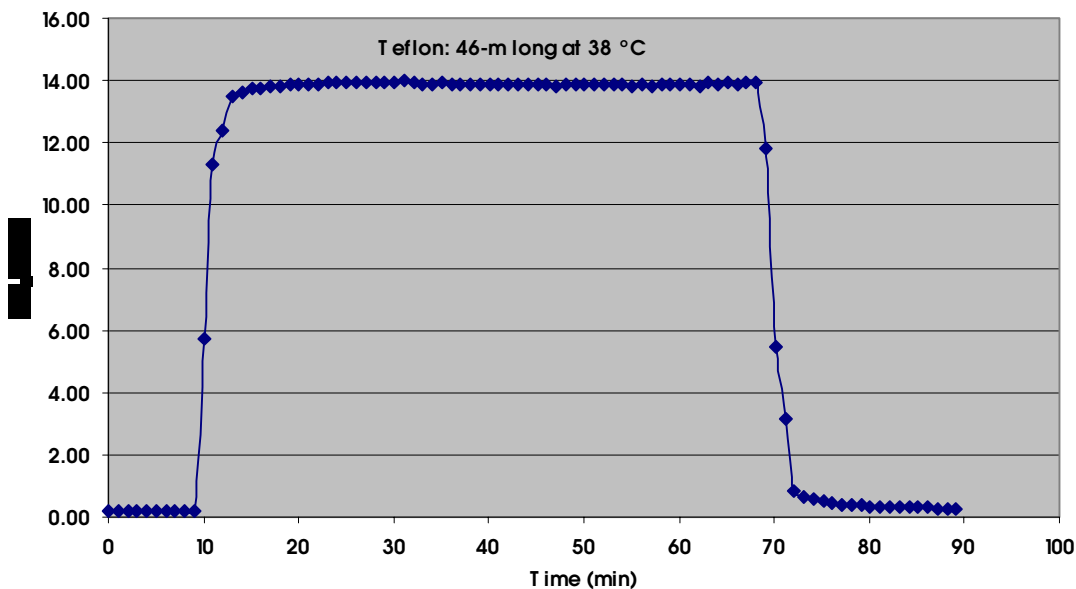
Figure 1. Example of warm-up (0-10 min), adsorption (11-70 min) and desorption (71-90 min) stages during one trial for a 46-m long Teflon tubing maintained at 38 ^{O}C.

A LabVIEW program was also developed to record the information from the analyzer using National Instruments hardware and software. This program updated and recorded data every five seconds, twice the update rate of the analyzer and 12 times the logging rate of the analyzer. The faster update rate ensured that every point from the analyzer was recorded. The five second data were averaged over one minute. In addition to the ammonia concentration, the logging program stored the date, time, ammonia flow rate, and air flow rate. The variables tested in this experiment are outlined in Table 1.

Table 1. Ammonia adsorption variables tested

Treatment	Description of Variables
Material	Teflon
Temperature (C)	26.67 and 37.78
Length (m)	15.24 and 45.72
Inlet Concentration (ppm)	2, 5, 10,15, 25, and 35
Treatment	**Description of Variables**
Material	LDPE
Temperature (C)	26.67 and 37.78
Length (m)	15.24 and 45.72
Inlet Concentration (ppm)	5 and 15

For this study three replications per trials were used, bringing the total number of experiments to 96. As shown in Table 1, extra concentrations were used for Teflon to model ammonia adsorption over a larger range, as Teflon is typically used to convey ammonia more frequently (Kosmulski, 2001). The ideal concentration is used for display purposes:

To change the temperature for each experiment, the entire length of tubing (not including inlets or outlets) was placed in an incubator. To ensure accuracy in these experiments the temperature inside the tubing was determined by using stainless steel temperature probes inserted into the tubing exiting from the incubator. Warm air was drawn through the bottom of the incubator and across a heating element. The air was then passed across the different lengths of tubing, warming the interior mixture. After determining the internal temperature and respective incubator setting, the temperature controls could be accurately described. A data logger (Onset Communications, Bourne, Ma.) was used to record the temperature information as well as the time required to attain each temperature. Software created by Onset Communications (BoxCar Pro 4.0) was used to read the temperatures from the data loggers. The actual, not ideal, output temperatures, lengths, and inlet and outlet ammonia concentrations were used in the statistical analysis

Results and Discussion

As described earlier, ammonia adsorption to Teflon and LDPE tubing was measured for two lengths, two temperatures, and 6 ammonia inlet concentrations for Teflon and 2 ammonia inlet concentrations for LDPE. Tables 2 and 3 present ammonia adsorption results for Teflon and LDPE, respectively. Actual ammonia inlet and outlet concentrations and their differences (adsorption) along with their standard deviations are presented in these tables. For Teflon, adsorption of ammonia generally increased slightly within the same inlet concentration as the temperature of the tubing increased, regardless of the difference in the length of tubing (Table 2). Among Teflon inlet concentrations, regardless of different temperatures and lengths of the tubing, ammonia adsorption was generally one ppm or less, well within the measurement sensitivity (± 2% of the 0-100ppm measuring scale) of the ammonia analyzer. On the other hand, ammonia adsorption for the LDPE tubing (Table 3) increased with increasing inlet concentration, temperature and length of the tubing. The lowest adsorption (0.84 ppm) was observed for the inlet concentration that corresponded to the ideal concentration of 5 ppm at lower temperature (25.2 ^{O}C) and smaller length (14.8-m), while the highest adsorption (3.58 ppm) was observed for the inlet concentration that corresponded to the ideal concentration of 15 ppm at higher temperature (37.7 ^{O}C) and higher length (45.3-m).

Table 4 presents the analysis of variance results for mean values of ammonia adsorption (C_{Diff}) as a function of inlet concentrations, tubing lengths, temperatures and tubing material for Teflon and LDPE. Fisher's least significant difference statistics was used to compare mean adsorption. For Teflon, ammonia adsorption for 15 ppm ideal inlet concentration was significantly higher than those for 5, 25 and 35 but statistically similar to all other ideal inlet concentrations. Also Teflon ideal inlet concentrations of 2, 5, 10, 25, and 35 ppm had statistically similar mean adsorptions. For LDPE, mean adsorption at ideal inlet concentration of 15 ppm was significantly higher than that for the ideal inlet concentration of 5ppm. Generally, longer Teflon and LDPE tubing at higher temperatures resulted in higher ammonia adsorption but none of the means for either tubing were statically different due to higher temperatures or greater lengths. Mean adsorption (compared at 5 and 10 ppm ideal inlet concentrations) for LDPE was higher than that for Teflon.

Table 2. Ammonia adsorption results for Teflon

C_{ideal} (ppm)	Temp. ^{o}C	Length (m)	Inlet C ppm	(S.D.)*	Outlet C ppm	(S.D.)*	Difference ppm	(S.D)*
2	25.2	15.5	2.30	(0.04)	1.10	(0.08)	1.20	(0.09)
2	25.6	46.6	1.80	(0.01)	0.96	(0.10)	0.84	(0.10)
2	36.7	15.5	2.30	(0.05)	1.09	(0.04)	1.21	(0.08)
2	37.7	46.6	2.00	(0.01)	0.98	(0.06)	1.02	(0.07)
5	25.2	15.5	5.00	(0.10)	4.81	(0.16)	0.19	(0.14)
5	25.6	46.6	4.80	(0.07)	4.12	(0.15)	0.68	(0.22)
5	36.7	15.5	5.40	(0.09)	4.72	(0.04)	0.68	(0.06)
5	37.7	46.6	4.60	(0.10)	3.75	(0.21)	0.85	(0.20)
10	25.2	15.5	10.20	(0.32)	9.12	(0.07)	1.08	(0.33)
10	25.6	46.6	9.60	(0.21)	8.94	(0.09)	0.66	(0.25)
10	36.7	15.5	10.50	(0.33)	9.13	(0.12)	1.37	(0.33)
10	37.7	46.6	9.80	(0.03)	9.05	(0.16)	0.75	(0.14)
15	25.2	15.5	15.10	(0.27)	14.24	(0.79)	0.86	(1.00)
15	25.6	46.6	14.40	(0.13)	13.27	(0.84)	1.13	(0.75)
15	36.7	15.5	15.30	(0.33)	13.10	(0.58)	2.20	(0.34)
15	37.7	46.6	14.60	(0.27)	13.38	(0.52)	1.22	(0.78)
25	25.2	15.5	24.50	(0.27)	24.15	(0.26)	0.35	(0.23)
25	25.6	46.6	24.20	(0.06)	24.08	(0.07)	0.12	(0.04)
25	36.7	15.5	25.30	(0.50)	24.35	(0.11)	0.95	(0.40)
25	37.7	46.6	24.90	(0.29)	24.07	(0.15)	0.83	(0.44)
35	25.2	15.5	34.40	(0.41)	34.27	(0.46)	0.13	(0.05)
35	25.6	46.6	35.60	(0.33)	33.70	(0.26)	1.90	(0.44)
35	36.7	15.5	34.43	(0.20)	34.28	(0.07)	0.15	(0.19)
35	37.7	46.6	35.20	(0.92)	34.19	(0.19)	1.01	(0.92)

*n=3

Table 3. Ammonia adsorption results for LDPE

C_{ideal} (ppm)	Temp. ^{o}C	Length (m)	Inlet C ppm	(S.D.)*	Outlet C ppm	(S.D.)*	Difference ppm	(S.D.)*
5	25.2	14.8	5.1	(0.14)	4.26	(0.10)	0.84	(0.22)
5	25.6	45.3	4.8	(0.07)	3.5	(0.36)	1.30	(0.31)
5	36.6	14.8	5.4	(0.10)	4.05	(0.08)	1.35	(0.16)
5	37.7	45.3	4.9	(0.10)	3.16	(0.12)	1.74	(0.16)
15	25.2	14.8	15.1	(0.34)	12.71	(0.40)	2.39	(0.07)
15	25.6	45.3	14.4	(0.19)	11.72	(0.27)	2.68	(0.43)
15	36.6	14.8	15.4	(0.32)	12.43	(0.49)	2.97	(0.63)
15	37.7	45.3	14.7	(0.29)	11.12	(0.35)	3.58	(0.60)

*n=3

Table 4. Effect of inlet concentration, temperature, length, and material on ammonia adsorption to Teflon and LDPE.

	Inlet Concentration Ideal ppm	Mean ppm	Length m	Mean C_{Diff} ppm	Temp. C	Mean C_{Diff} ppm	Material	Mean C_{Diff} ppm
Teflon	2^{1}	1.07^{ab*}	15.2^{2}	0.86^{a}	26.7^{2}	0.76^{a}		
	5	0.60^{a}	45.7	0.92^{a}	37.8	1.02^{a}		
	10	0.96^{ab}						
	15	1.35^{b}						
	25	0.56^{a}						
	35	0.80^{a}						
LDPE	5^{1}	1.31^{a}	15.2^{1}	1.90^{a}	26.7^{1}	1.80^{a}		
	15	2.90^{b}	45.7	2.32^{a}	37.8	2.41^{a}		
Teflon vs. LDPE							$Teflon^{3}$	0.98^{a}
							LDPE	2.11^{b}

[1] n=12 per treatment mean for Teflon concentration, LDPE concentration, LDPE length, and LDPE Temperature
[2] n=36 per treatment for Teflon length and Teflon temperature
[3] n=24 per treatment for Teflon vs. LDPE
* Mean C_{Diff} values in columns followed by different letters are different at a 5% level

Multiple linear regressions were performed for both materials to model the adsorption of ammonia. Tubing length of 15.2 or 45.7 meters did not statistically affect the adsorption of ammonia onto Teflon tubing. Tubing length was significant for LDPE within the experimental ranges tested (at $\alpha=0.05$). The inlet concentrations (C_{in}) used for the two different materials were also significant in explaining adsorption. An intercept was not significant in the regression modeling for Teflon; however, it was significant in the modeling of LDPE. The linear regressions for Teflon and LDPE are displayed in Equations 5 and 6 below. The standard error and p-values for the variables are outlined in Table 5.

$$C_{TEFLON} = 0.031 \cdot T + 0.994 \cdot C_{in} \tag{5}$$

$$C_{LDPE} = -1.791 + 0.058 \cdot T\ 0.014 + 0.19 \cdot L + 1.193 \cdot C_{in} \tag{6}$$

Table 5. Tests for variable significance

Material	Variable	Estimate	Standard Error	t-Stat	p-Value
Teflon	T	0.031	0.005	6.128	b
	C_{in}	0.994	0.009	114.036	a
LDPE	L	-1.791	0.305	-5.876	b
	C_{in}	0.058	0.008	6.816	b
	T	0.019	0.003	5.791	b
	Intercept	1.193	0.012	98.777	a

a: $\alpha \ll 0.001$; b: $\alpha < 0.001$

Conclusions

This paper quantifies the adsorption of ammonia onto Teflon and LDPE tubing under different length, temperature, and inlet ammonia concentrations. After analyzing the data, several statistical analyses were conducted. Ammonia adsorption on Teflon was statistically less than LDPE. Tubing length was not significant in modeling ammonia adsorption onto Teflon, but was significant for LDPE. There were significant differences between inlet and outlet concentrations of LDPE at 5 and 15 ppm. Overall, ammonia adsorption to Teflon was nearly 1ppm regardless of the magnitude of inlet concentration, temperature or length of tubing. This loss on to the Teflon surface was well within the measurement sensitivity of the ammonia analyzer. Using linear regression, predictive equations were developed to model the adsorption of ammonia under similar conditions to those tested in the laboratory. Care should be taken with extrapolation of data. For example, if the source (inlet) temperature was 3 ^{o}C and the measured concentration was 20 PPM, Equation 5 would estimate that the source (inlet) ammonia concentration was actually less than the outlet (measured). These impossible situations will occur when predictive equations are misused. The complex interactions of adsorption require exponential experimental design growth beyond the limits of this study. The focus of this work was to begin the difficult task of clearly defining the treatments that have statistical impact on adsorption; future work is required to expand and refine this research.

FUTURE WORK

This experiment assumes that the changes in ammonia adsorption are a linear function of the different variables tested. This may not be necessarily true, but under the small range of values encountered in the field coupled with limited time, this assumption was determined to be valid. Extrapolation / interpolation of this data have not been physically verified, and deserve attention to strengthen the model and investigate other predictors. Other factors may play a role in determining the true variables that affect the adsorption of ammonia such as pressure, relative humidity, and gas flow rate. Future work should continue in this research to extend the knowledge base for ammonia adsorption.

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