

## Article

# Investigation of the Main Parameters Influencing the Kinetics of an Ammonia Stripping Plant Treating Swine Digestate

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**Abstract:** Ammonia stripping is a consolidated technology that can be adopted to reduce the excessive content of nitrogen in the digestate, thus allowing its reuse as fertilizer within the maximum nitrogen loads set by regulations. In this work, the role of the main operational parameters (airflow and temperature) was assessed on a pilot bubble reactor treating a swine-based digestate, under batch conditions. A kinetic model was developed to correlate temperature, airflow and the ammonia removal yield. Varying the temperature from 60 to 70 °C and the airflow rate from 30 to 60 m<sup>3</sup><sub>air</sub> h<sup>-1</sup> m<sup>-3</sup><sub>digestate</sub>, the performance of the plant was measured at different reaction times. The process was favored by the spontaneous pH increase over 10, without basifying agent addition. The lowest removal efficiency (50%) was recorded at 60 °C and 30 m<sup>3</sup><sub>air</sub> h<sup>-1</sup> m<sup>-3</sup><sub>digestate</sub>. A removal efficiency higher than 80% was reached running the process at 70 °C and 45 or 60 m<sup>3</sup><sub>air</sub> h<sup>-1</sup> m<sup>-3</sup><sub>digestate</sub>. Performance curves were then developed as a practical tool to identify the operating conditions leading to a desired nitrogen removal rate: for instance, under the most severe conditions, up to 80% ammoniacal nitrogen could be removed in about 10 h. Though the obtained results are valid for the treated digestate, the experimental methodology as well as the mathematical model could be replicated in other case studies, thus allowing the amelioration of the process operation.



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**Keywords:** ammonia stripping reactor; anaerobic digestion; nitrogen removal; livestock manure; performance curves

## 1. Introduction

Livestock manure management is a critical issue, especially in the case of large breeding farms. Manure contains valuable nutrients, such as nitrogen, phosphorus, potassium, micronutrients (copper, manganese, zinc, etc.) [1], and it is a source of organic matter, making it a useful soil fertilizer [2]. The total nitrogen content of animal manure is generally between 6 (for cattle and goat) and 30 kg ton<sup>-1</sup> (for broiler) [1]. Animal manure application as fertilizer is expected to improve soil quality, and to affect crop productivity [3,4]. However, manure also contains pathogens and other pollutants, such as pharmaceutical residues [5], and needs to be pre-treated before land spreading [6]. Moreover, manure can be considered as an environmental pollutant when it is over-applied to cropland, and a source of pollution following runoff into surface water [7,8]. The characteristics of manures, in terms of nutrient and organic matter contents, however, vary greatly, thus their properties should be attentively monitored for safe use in agricultural soils [9]. When nitrogen inputs exceed crop needs, excessive amounts of nitrate (N-NO<sub>3</sub><sup>-</sup>) may enter either ground or surface water [7]. The Nitrates Directive (91/676/EEC) [10] has been established to protect the water quality from pollution originated by agricultural sources, and to foster the use of good farming practices. The Directive requires member states to establish Nitrate Vulnerable Zones (NVZs), defined as those areas which drain into the

waters that, due to agricultural activities, are eutrophic or could contain a concentration of more than  $50 \text{ mg L}^{-1}$  of  $\text{NO}_3^-$  [10], also considering the specific geographical and geomorphological characteristics of the area. In Italy, this regulation was transposed with the Ministerial Decree 19 April 1999 (code of good agricultural practice) [11], the Legislative Decree 3 April 2006 n. 152 and subsequent modifications [12], and the Ministerial Decree 25 February 2016 [13], introducing criteria, restrictions and limitations for organic fertilisation. A maximum limit of  $170 \text{ kg ha}^{-1} \text{ year}^{-1}$  of N from organic manure was established for NVZs, whereas in the case of non-vulnerable areas the limit was set as  $340 \text{ kg ha}^{-1} \text{ year}^{-1}$ , as average [14].

As a consequence, in addition to other treatments such as anaerobic digestion (AD), ammonia removal is advisable from digestate destined for soil spreading, both for ammonia recovery as a valuable resource and for the nitrogen content reduction. Different technologies exist for ammonia removal [15,16], ammonia stripping being one of the most commonly applied [17]. In this process, ammonia is removed from the liquid fraction by flowing air through the bulk. This technology has been successfully applied to digestate [17–19], landfill leachate [20,21], and wastewater [22]. Alkali addition may be required in order to raise the pH and optimize the process, which involves expenses for the chemicals [23]. The parameters mainly affecting ammonia stripping were identified as the temperature and pH of the liquid, as well as the airflow rate, the liquid characteristics also playing a relevant role [17,24,25]. Commonly, stripping towers or packed columns are used, where packing materials are employed to enhance the mass transfer between the liquid and gaseous phases. Nevertheless, these technologies have some limitations, such as the consumption of energy for heating the digestate, alkali to adjust the pH, scaling and fouling (due to the formation of calcium carbonate on the surface of packing materials), which can affect ammonia removal efficiencies over time [16,24]. To overcome some of these disadvantages, alternative technologies such as jet loop and aero-cyclone reactors [24], semi-batch jet loop reactors [26], water spray reactors [27], and air bubble reactors [18,28] are being implemented and studied. In particular, bubble reactors have the main advantage of not being sensitive to fouling, and it has been demonstrated that, working under sufficiently high temperature (above  $60 \text{ }^\circ\text{C}$ ), the dosage of alkaline reagents may be prevented [18]. This technology has been successfully used for leachate and digestate treatment. Finally, ammonia stripping could be conveniently combined with AD, as the thermal energy required to reach the high temperatures favoring the process can be provided by the biogas (fed to a boiler or a combined heat and power (CHP) unit).

The objectives of this study were to test the performance of an ammonia stripping bubble reactor on a swine digestate, to assess the role of the main parameters (temperature, pH, airflow rate), and, in turn, to find the conditions to better manage the process. While ammonia stripping in packed columns is a well-established technology, the use of air bubble reactors, for these specific applications, is a quite novel and promising solution, due to the big advantage of avoiding trouble due to fouling. However, in the scientific literature, the performance of this technology for digestate treatment, under several operating conditions, is still scarce, leaving room for further investigation. In the present work, the experimentation was carried out on a pilot plant working under batch conditions. The correlation found among stripping efficiency and the process parameters and the developed mathematical model may contribute to fill the knowledge gap on the application to real substrates (wastewater, digestate, livestock manure, landfill leachate, etc.), thus fostering the diffusion of this effective technology and improving the management practices of swine digestates and resource recovery.

## 2. Materials and Methods

### 2.1. The Ammonia Stripping Pilot Plant

The bubble reactor pilot plant used in the experiment consists of (Figure 1):

- a stripping reactor;
- an air blower;

- a heating system (an oil-fired boiler and a tube-in-tube heat exchanger);
- pipes and pumps for handling the digestate and heating water;
- a process control and monitoring system.

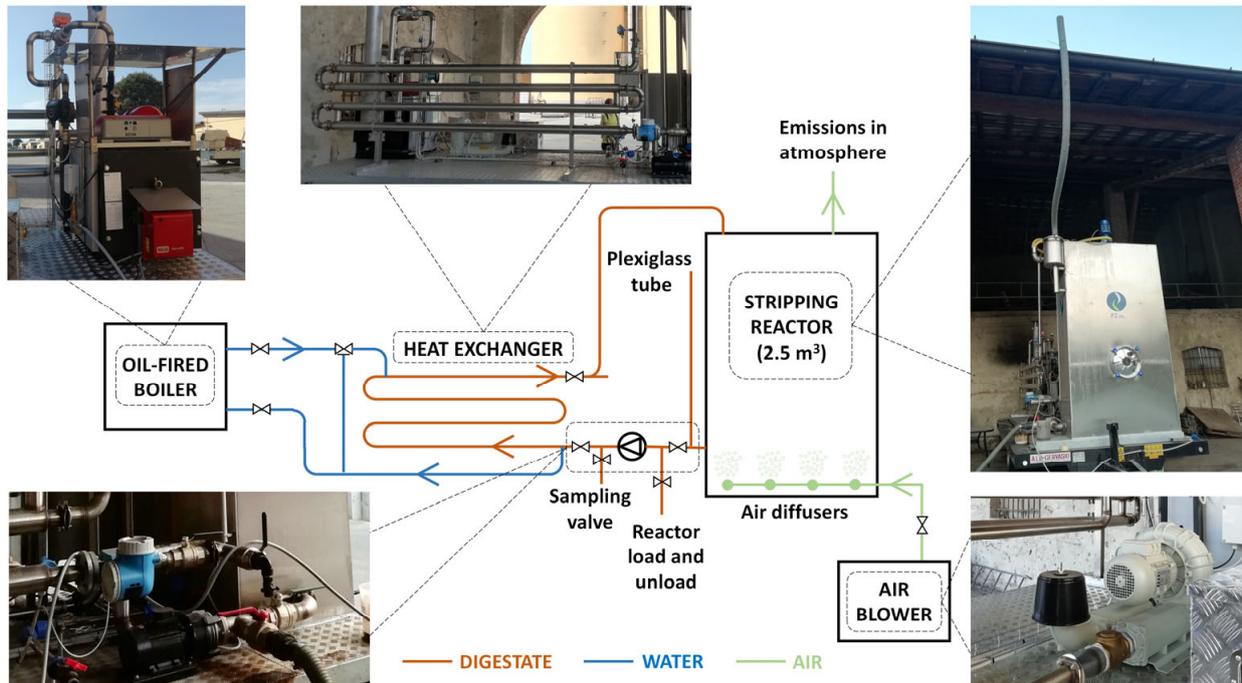


Figure 1. Scheme of the pilot reactor used for the experiments.

The stripping reactor volume is 2.5 m<sup>3</sup>; the net usable volume, which considers the space occupied by the foam created by air insufflation, is approximately 1.5 m<sup>3</sup>. At the top of the reactor a foam-breaking turbine is installed. The gas, enriched with the ammonia stripped from the treated digestate, is conveyed into the atmosphere. A sampling valve for the collection of the samples is positioned downstream of the circulation pump. The reactor is equipped with a plexiglass tube for the measurement of the digestate level, and with an equipment to collect the overloading foam which is recirculated into the reactor.

A blower with a capacity of 112 m<sup>3</sup> h<sup>-1</sup> at 2500 rpm supplies the process air inside the stripping reactor. Height perforated tubes (air diffusers) are installed at a height of approximately 20 cm from the bottom of the stripping reactor. A flowmeter and a gate valve are installed on the air supply pipe.

A heating system is used to reach and maintain the temperature of the digestate at the set value. An oil-fired boiler heats the water, which is fed to the tube-in-tube heat exchanger. The digestate is pumped from the bottom of the stripping reactor into the DN50 inner pipes of the heat exchanger, while the hot water flows through the DN80 outer jacket. From the heat exchanger, the digestate and the water return to the stripping reactor and the boiler circuit, respectively. The heating system is completed by a three-way valve to regulate the flow of water to the exchanger, two flow meters (for water and digestate, respectively), and four temperature sensors.

A first control panel is used to switch the equipment serving the plant on and off. A second control panel is used to set the temperature of the digestate in the reactor and the airflow rate. This panel records the data and displays the main process parameters: the temperature of water and of digestate entering and leaving the heat exchanger; the digestate flow rate entering to the heat exchanger (the water flow rate can be read directly on the meter display); the degree of opening of the hot water three-way valve; and the airflow rate.

## 2.2. Tested Conditions and Experimental Procedure

We conducted nine tests in batch (named from A to I): three temperatures (T) (60, 65, 70 °C) and three airflow rates ( $Q_{\text{air}}$ ) (45, 68, 90  $\text{m}^3_{\text{air}} \text{h}^{-1}$ , corresponding to 30, 45, 60  $\text{m}^3_{\text{air}} \text{h}^{-1} \text{m}^{-3}_{\text{digestate}}$ ) were tested (Table 1). All tests lasted 12 h, with the exception of test G, which lasted 8 h. These conditions were selected based on previous research conducted on a full-scale plant [18].

**Table 1.** Operating conditions of the stripping tests: temperature (T) and airflow rates ( $Q_{\text{air}}$ ).

Test	T (°C)	$Q_{\text{air}}$ ( $\text{m}^3_{\text{air}} \text{h}^{-1} \text{m}^{-3}_{\text{digestate}}$ )
A	60	30
B	65	30
C	70	30
D	60	45
E	65	45
F	70	45
G	60	60
H	65	60
I	70	60

The digestate tested in the experimental study came from an anaerobic digester serving a farm, treating a mixture of pig slurry and maize mash. The main characteristics of digestate are reported in Table 2.

**Table 2.** Main characteristics of digestate.

Parameter	Unit of Measurement	Value
pH	-	8.2–9.1
Ammoniacal nitrogen ( $\text{N-NH}_4^+$ )	( $\text{mg L}^{-1}$ )	2090–2450
Total Nitrogen (TN)	( $\text{mg L}^{-1}$ )	2350–3050
Total solids (TS)	(%)	2.03–2.61
Volatile solids (VS)	(%)	1.17–1.68
Total Phosphorus (TP)	( $\text{mg L}^{-1}$ )	695–1095

Each test was conducted as follow:

- the reactor was loaded with 1.5  $\text{m}^3$  of digestate and the digestate level measured;
- the digestate circulation pump was switched on in order to homogenize the digestate content in the system;
- after 10 min, at time 0 h, one digestate sample was collected from the sampling valve;
- the test temperature and the airflow rate were set, and the boiler, water circulation pump and foam-breaking turbine were switched on;
- six digestate samples were collected from the tap at times: 0.5 h; 1 h; 2 h; 4 h; 6 h; 8 h; and 12 h. The temperature and flow rate of the water and digestate were monitored during the whole test;
- at the end of the test, the digestate level was measured again, to estimate the water loss from the system as a result of the release of water-saturated gas into the atmosphere.

The pH, ammoniacal nitrogen ( $\text{N-NH}_4^+$ ) and total nitrogen (TN) were analyzed in all samples by an external laboratory. The following analytical methods were used to determine pH,  $\text{N-NH}_4^+$  and TN respectively: CNR IRSA 1 Q 64 Volume 3, 1985, CE Regulation 2003/2003 13/10/03 Official Gazette CE L304 21/11/03 Annex IV, MPI-216-R00.19.

### 2.3. Ammonia Stripping Efficiency

The theoretical ammonia removal rate ( $\eta$ ) was calculated as (1):

$$\eta = \frac{(N - NH_4^+)_{0} - (N - NH_4^+)_{end}}{(N - NH_4^+)_{0}} \quad (1)$$

where  $(N - NH_4^+)_{0}$  and  $(N - NH_4^+)_{end}$  are the ammoniacal nitrogen concentration at the beginning and at the end of the test. As the value at the beginning of the test, we considered the concentration measured in the sample collected at time 0.5 h (the value in the sample collected at time 0 h was excluded because it showed anomalous value in most of the tests, probably due to the insufficient homogenization time of the digestate in the reactor).

During each test, evaporation of the digestate occurred to some extent. Therefore, the real process performance ( $\eta'$ ) was calculated, based on a mass balance, as (2):

$$\eta' = \frac{((N - NH_4^+)_{0} \cdot V_0) - ((N - NH_4^+)_{end} \cdot (V_0 - V_{lost}))}{(N - NH_4^+)_{0} \cdot V_0} \quad (2)$$

where:  $V_0$  is the initial volume of the digestate in the reactor, equal to 1.5 m<sup>3</sup>, and  $V_{lost}$  is the volume of digestate lost during the test and measured through the difference in the level of the liquid in the reactor.

The theoretical and the real removal of total nitrogen (TN) were calculated according to Equations (1) and (2), respectively, with TN concentrations instead N-NH<sub>4</sub><sup>+</sup> ones.

### 2.4. Modelling the Ammonia Decay

For each test, time intervals were identified in which both pH and temperature were approximately constant. With the airflow rate also constant, it was possible to describe the batch test kinetic with a simple mathematical model (3), by assuming a first order reaction with respect to ammoniacal nitrogen:

$$(N - NH_4^+)_{t} = (N - NH_4^+)_{0} \cdot e^{-kt} \quad (3)$$

where:  $(N - NH_4^+)_{t}$  and  $(N - NH_4^+)_{0}$  are the ammoniacal nitrogen concentration at time  $t$  and at initial time (mg L<sup>-1</sup>), respectively;  $t$  is the time (h); and  $k$  is the reaction rate constant (h<sup>-1</sup>).

In each interval, the value of the reaction rate constant was therefore calculated using the Excel (Microsoft 2010) solver, in order to minimize the deviation between the experimental data and the corresponding values calculated using Equation (3). Based on the obtained results, two graphs were created showing, respectively, the influence of the temperature and of the airflow rate, on the ammonia removal rate. Results were then approximated with straight line equations, which linked the value of  $k$  to the temperature and to the airflow rate.

By combining Equations (1) and (3), the following expression (4) can be obtained to correlate ammonia removal efficiency and the reaction rate  $k$ :

$$\eta(t) = 1 - \frac{(N - NH_4^+)_{t}}{(N - NH_4^+)_{0}} = 1 - e^{-kt} \quad (4)$$

By replacing  $k$  in Equation (4) with the equations that approximate the lines, we constructed process performance curves permitting, at the airflow rates tested, determination of the time required to achieve the desired performance by setting different stripping temperatures.

### 3. Results

#### 3.1. The Experimental Study

The results of conducted tests are reported in Table 3.

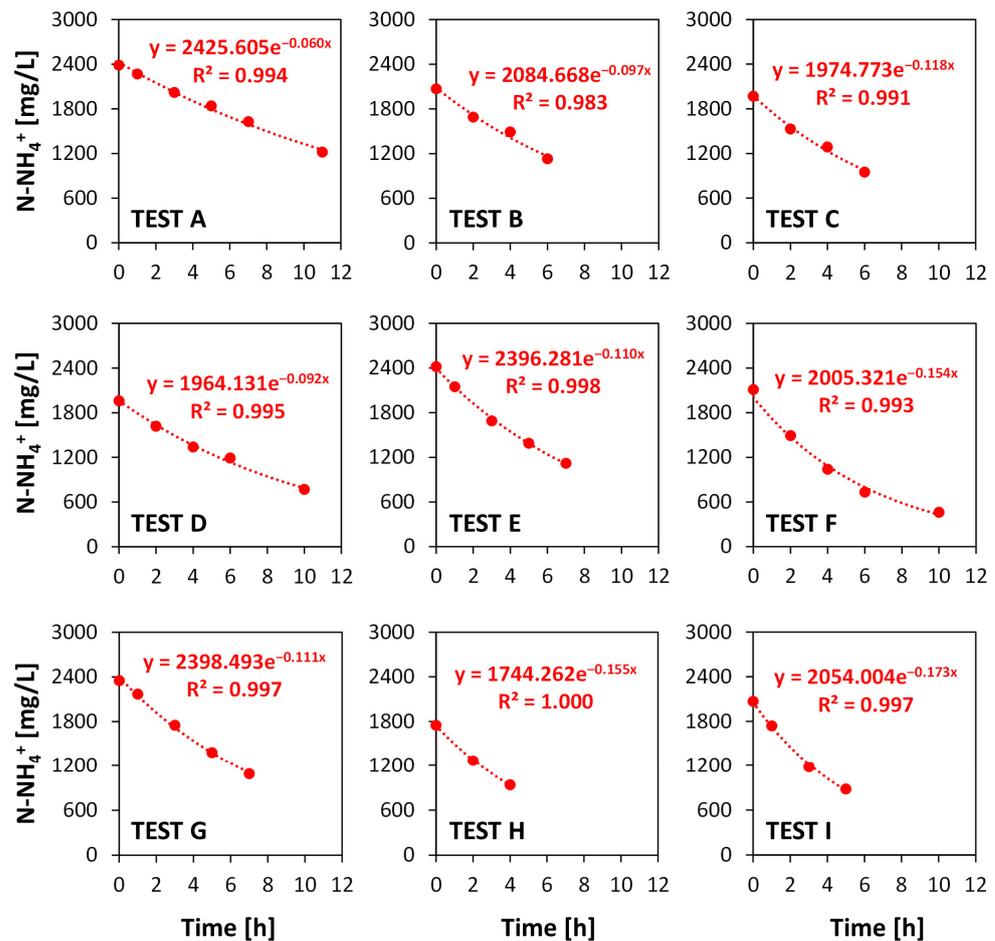
**Table 3.** pH, ammoniacal nitrogen (N-NH<sub>4</sub><sup>+</sup>) and total nitrogen (TN) measured in all the samples taken during the experiments and operating conditions of temperature (T) and airflow rate (Q<sub>air</sub>). In grey, the intervals identified in which both pH and temperature were considered approximately constant (n.a.: not available).

Test	Q <sub>air</sub> (m <sup>3</sup> <sub>air</sub> h <sup>-1</sup> m <sup>-3</sup> <sub>digestate</sub> )	T (°C)	Parameter	Time (h)							
				0	0.5	1	2	4	6	8	12
A		60	pH	8.70	8.93	9.31	9.71	9.94	10.09	10.16	10.14
			N-NH <sub>4</sub> <sup>+</sup> (mg L <sup>-1</sup> )	1600	2350	2390	2270	2020	1840	1630	1220
			TN (mg L <sup>-1</sup> )	2380	3050	3030	2960	2750	2430	2390	2050
B	30	65	pH	8.60	8.87	9.38	9.76	10.01	10.14	10.17	10.12
			N-NH <sub>4</sub> <sup>+</sup> (mg L <sup>-1</sup> )	2070	2240	2160	2070	1690	1490	1130	540
			TN (mg L <sup>-1</sup> )	3040	2640	2410	2380	2080	1900	1740	1330
C		70	pH	8.32	8.88	9.37	9.85	10.04	10.07	10.05	9.92
			N-NH <sub>4</sub> <sup>+</sup> (mg L <sup>-1</sup> )	2200	2230	2150	1970	1530	1290	950	770
			TN (mg L <sup>-1</sup> )	3020	2800	2830	2540	2210	2060	1580	1110
D		60	pH	8.20	8.82	9.30	9.78	9.80	9.98	9.91	9.85
			N-NH <sub>4</sub> <sup>+</sup> (mg L <sup>-1</sup> )	2100	2090	2320	1960	1620	1340	1190	770
			TN (mg L <sup>-1</sup> )	2980	2830	2600	2120	2030	1850	1640	1080
E	45	65	pH	8.30	9.03	9.36	9.83	10.05	10.13	10.12	9.98
			N-NH <sub>4</sub> <sup>+</sup> (mg L <sup>-1</sup> )	2440	2450	2420	2150	1690	1390	1120	850
			TN (mg L <sup>-1</sup> )	3050	2980	2770	2490	2160	1870	1460	1160
F		70	pH	8.63	9.25	9.76	10.20	10.30	10.38	10.32	10.13
			N-NH <sub>4</sub> <sup>+</sup> (mg L <sup>-1</sup> )	2580	2430	2410	2110	1490	1040	730	460
			TN (mg L <sup>-1</sup> )	3190	3050	2830	2530	2080	1250	1100	970
G		60	pH	9.07	9.08	9.57	9.93	10.15	10.23	10.17	n.a.
			N-NH <sub>4</sub> <sup>+</sup> (mg L <sup>-1</sup> )	1120	2230	2350	2170	1750	1380	1090	n.a.
			TN (mg L <sup>-1</sup> )	1760	2740	2820	2640	1920	1730	1360	n.a.
H	60	65	pH	9.12	8.82	9.15	9.59	9.93	10.11	10.01	9.85
			N-NH <sub>4</sub> <sup>+</sup> (mg L <sup>-1</sup> )	1350	2290	2330	1970	1750	1270	940	640
			TN (mg L <sup>-1</sup> )	1470	2350	2590	2250	1890	1520	1340	940
I		70	pH	8.38	9.40	9.82	10.04	10.11	9.88	9.50	8.63
			N-NH <sub>4</sub> <sup>+</sup> (mg L <sup>-1</sup> )	2240	2250	2070	1740	1180	880	700	520
			TN (mg L <sup>-1</sup> )	3130	2880	2600	2340	2030	1860	1750	1520

In almost all tests, it took about one hour to reach the set temperature (Figure S1, Supplementary Materials), with the two exceptions of tests C and H, during which almost 2 h were necessary to reach the temperature of 70 and 65 °C, respectively. Once reached, the set temperature was kept constant during the whole duration of the test. In test H, a failure to a pump occurred that needed to be repaired.

The pH of the digestate entering the reactor ranged from a minimum of 8.2 (test D) to a maximum of 9.12 (test H). After 12 h, the pH reached values ranging between 9.85 and 10.14, except for test G, where the value of 10.17 was reached after 8 h, and test I, where the pH anomalously decreased from 9.50 (8 h) to 8.63 (12 h). It was observed that the pH increased during the first part of all tests (between 2 and 4 h), to then remain stable at a value of about 10, with the only exception of test I, as mentioned above.

Decreasing trends of N-NH<sub>4</sub><sup>+</sup> concentration during all tests (concentrations marked with grey background in Table 3) are shown in Figure 2, together with the trendlines according to kinetic Equation (3). Removal efficiencies are summarized in Table 4.



**Figure 2.** Trends of ammoniacal nitrogen ( $\text{N-NH}_4^+$ ) concentration during the nine tests and trendlines, according to kinetic Equation (3).

**Table 4.** Theoretical ( $\eta$ ), Equation (1) and real ( $\eta'$ ), Equation (2) ammoniacal nitrogen ( $\text{N-NH}_4^+$ ) and total nitrogen (TN) removal efficiencies calculated in each test, at tested temperatures (T) and airflow rates ( $Q_{\text{air}}$ ).

Test	T (°C)	$Q_{\text{air}}$ ( $\text{m}^3_{\text{air}} \text{h}^{-1} \text{m}^{-3}_{\text{digestate}}$ )	$V_{\text{lost}}$ (L)	$\text{N-NH}_4^+$		TN	
				$\eta$ (%)	$\eta'$ (%)	$\eta$ (%)	$\eta'$ (%)
A	60	30	45	48.1	49.6	32.8	34.8
B	65		60	75.9	76.9	49.6	51.6
C	70		76	65.5	67.2	60.4	62.4
D	60	45	67	63.2	64.8	61.8	63.5
E	65		109	65.3	67.8	61.1	63.9
F	70		210	81.1	83.7	68.2	72.6
G	60	60	98	51.1	54.3	50.4	53.6
H	65		220	72.1	76.2	60.0	65.9
I	70		260	76.9	80.9	47.2	56.4

In test A,  $\text{N-NH}_4^+$  decreased from approximately  $2400 \text{ mg L}^{-1}$  to  $1200 \text{ mg L}^{-1}$ , with a removal yield of 49%, while total N decreased by 33%. In test B,  $\text{N-NH}_4^+$  decreased from about  $2200 \text{ mg L}^{-1}$  to  $540 \text{ mg L}^{-1}$ , with a removal yield of 76%, while total N decreased by 56%. In test C,  $\text{N-NH}_4^+$  decreased from approximately  $2200 \text{ mg L}^{-1}$  to  $770 \text{ mg L}^{-1}$  with a removal yield of 66%, while total N decreased by 63%. In test D,  $\text{N-NH}_4^+$  decreased from approximately  $2300 \text{ mg L}^{-1}$  to  $770 \text{ mg L}^{-1}$  with a removal yield of 67%, while total N decreased by 64%. In test E,  $\text{N-NH}_4^+$  decreased from approximately  $2400 \text{ mg L}^{-1}$  to

850 mg L<sup>-1</sup> with a removal yield of 65%, while total N decreased by 62%. In test F, N-NH<sub>4</sub><sup>+</sup> decreased from approximately 2600 mg L<sup>-1</sup> to 460 mg L<sup>-1</sup> with a removal yield of 82%, while total N decreased by 70%. In test G, N-NH<sub>4</sub><sup>+</sup> decreased from approximately 2300 mg L<sup>-1</sup> to 1090 mg L<sup>-1</sup> with a removal yield of 52%, while total N decreased by 50%. In test H, N-NH<sub>4</sub><sup>+</sup> decreased from approximately 2310 mg L<sup>-1</sup> to 640 mg L<sup>-1</sup> with a removal yield of 72%, while total N decreased by 60%. In test I, N-NH<sub>4</sub><sup>+</sup> decreased from approximately 2240 mg L<sup>-1</sup> to 520 mg L<sup>-1</sup> with a removal yield of 77%, while total N decreased by 51%.

Overall, the N-NH<sub>4</sub><sup>+</sup> initial concentration (at time 0.5 h) showed an average value of approximately 2300 mg L<sup>-1</sup>, with a maximum of 2450 mg L<sup>-1</sup> in test E, and a minimum of 2090 mg L<sup>-1</sup> in test D. The N-NH<sub>4</sub><sup>+</sup> decreased to values ranging from 1200 (test A) to 460 mg L<sup>-1</sup> (test F), with a theoretical removal yield ( $\eta$ ) ranging from 48% (test A) to 81% (test F) and a real efficiency ( $\eta'$ ) from 50% (test A) to 84% (test F). The TN showed a theoretical removal yield ( $\eta$ ) from 33% (test A) to 68% (test F) and a real removal yield ( $\eta'$ ) from 35% (test A) to 73% (test F).

### 3.2. Modelling the Stripping Performance

Table 5 reports the results of the calculation of the reaction rate constants, also shown in the equations of the trendlines in Figure 2. As explained above, only the values included in the time intervals where pH and temperature were considered approximately constant (highlighted in grey in Table 3) were used, so that a first order reaction, with respect to ammonia, could be assumed.

**Table 5.** Calculated rate constants (k), initial pH and ammoniacal nitrogen (N-NH<sub>4</sub><sup>+</sup>)<sub>0</sub> and respective operating conditions of temperatures (T) and airflow rates (Q<sub>air</sub>).

Test	T (°C)	Q <sub>air</sub> (m <sup>3</sup> <sub>air</sub> h <sup>-1</sup> m <sup>-3</sup> <sub>digestate</sub> )	pH <sub>0</sub>	pH Average	(N-NH <sub>4</sub> <sup>+</sup> ) <sub>0</sub> (mg L <sup>-1</sup> )	k (h <sup>-1</sup> )
A	60	30	8.70	10.00	2426	0.0602
B	65		8.60	10.04	2085	0.0971
C	70		8.32	10.02	1975	0.1179
D	60	45	8.20	9.88	1964	0.0916
E	65		8.30	9.99	2396	0.1096
F	70		8.63	10.28	2005	0.1539
G	60	60	9.07	10.09	2398	0.1111
H	65		9.12	10.04	1744	0.1554
I	70		8.38	10.01	2054	0.1733

The values of k ranged between a minimum of 0.0602 h<sup>-1</sup> (test A) and a maximum of 0.1733 h<sup>-1</sup> (test I). We can observe that, with pH on average equal to 10, the value of k only depends on temperature for a given flow rate value. Figures 3 and 4 show the effect of these two parameters. The most influential parameter is temperature: the slope of the lines in Figure 4 (around 0.006) is about three times greater with respect to those of the lines in Figure 3 (approximately 0.0018). Moreover, the two parameters are related to one another, given that the airflow rate influences the temperature.

When approximating the results with straight lines in Figure 4 and by applying Equation (4), we obtained the following expressions, for each airflow rate:

- for airflow rates equal to 30 m<sup>3</sup><sub>air</sub> h<sup>-1</sup> m<sup>-3</sup><sub>digestate</sub>

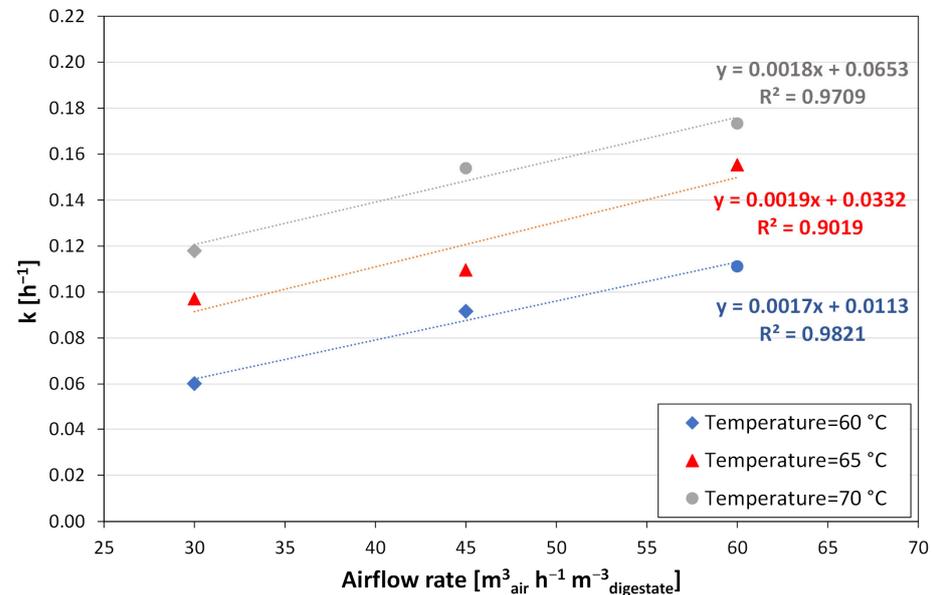
$$\eta(t) = 1 - e^{-(0.0058 \cdot T - 0.2833) \cdot t} \quad (5)$$

- for airflow rates equal to 45 m<sup>3</sup><sub>air</sub> h<sup>-1</sup> m<sup>-3</sup><sub>digestate</sub>

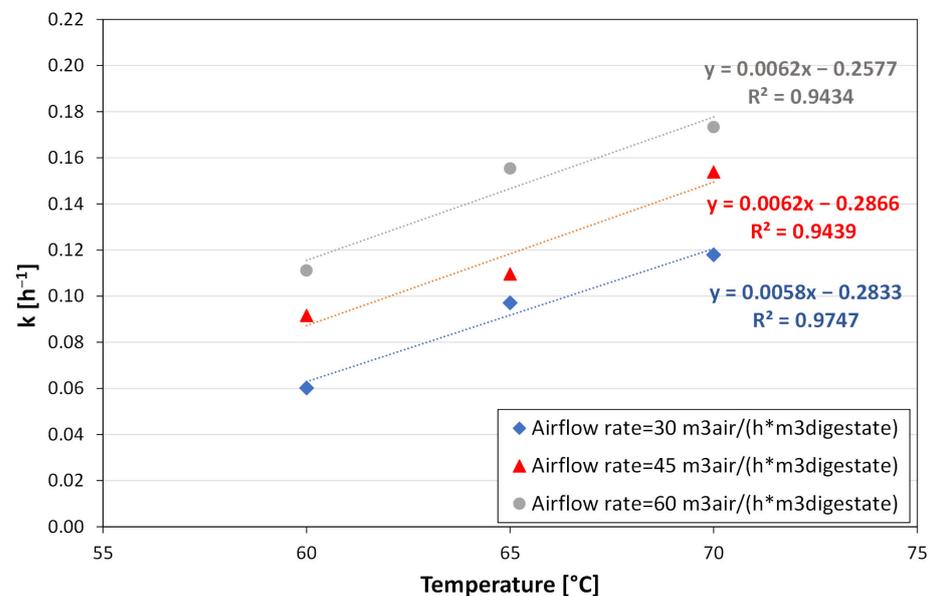
$$\eta(t) = 1 - e^{-(0.0058 \cdot T - 0.2833) \cdot t} \quad (6)$$

- for airflow rates equal to  $60 \text{ m}^3_{\text{air}} \text{ h}^{-1} \text{ m}^{-3}_{\text{digestate}}$

$$\eta(t) = 1 - e^{-(0.0062 \cdot T - 0.2577) \cdot t} \quad (7)$$

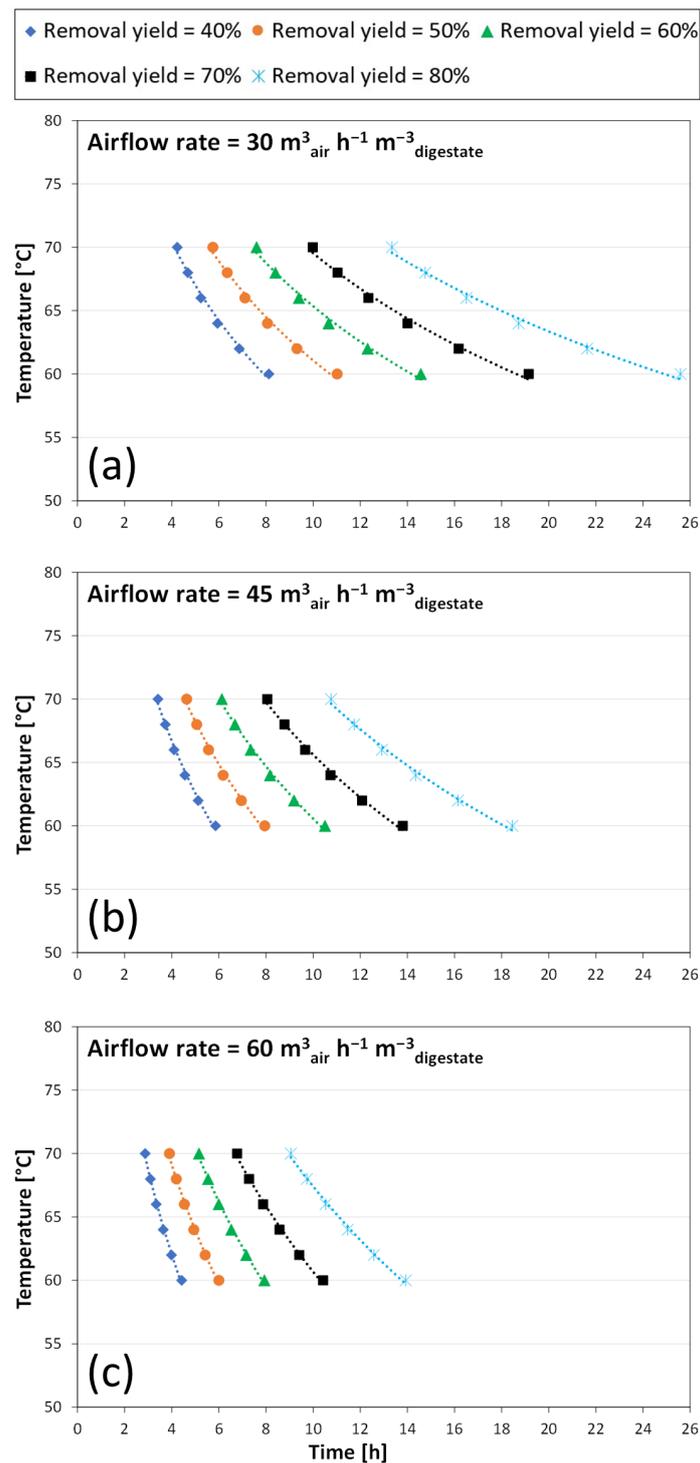


**Figure 3.** Effect of airflow rate on ammonia removal rate at different temperatures (pH~10).



**Figure 4.** Effect of digestate temperature on ammonia removal rate at different airflow rates (pH~10).

It was therefore possible, by setting different stripping temperatures, to calculate the time required to obtain the desired performance. The results of these calculations are summarised in Figure 5a–c, which shows the performance curves at the different airflow rates tested in the monitoring campaign. As an example, if operating with an airflow rate of  $30 \text{ m}^3_{\text{air}} \text{ h}^{-1} \text{ m}^{-3}_{\text{digestate}}$  and a temperature of  $65 \text{ }^{\circ}\text{C}$ , it would be necessary to treat the digestate for just over 10 h to obtain an efficiency of 60%. At the same airflow rate, but operating at a temperature of  $70 \text{ }^{\circ}\text{C}$ , almost 8 h would be sufficient to guarantee the same yield (Figure 5a). Alternatively, if operating with an airflow rate of  $60 \text{ m}^3_{\text{air}} \text{ h}^{-1} \text{ m}^{-3}_{\text{digestate}}$  and a temperature of  $70 \text{ }^{\circ}\text{C}$ , an efficiency of 80% could be reached in about 10 h (Figure 5c).



**Figure 5.** Performance curves for different airflows: respectively (a) 30 m<sup>3</sup> air h<sup>-1</sup> m<sup>-3</sup> digestate; (b) 45 m<sup>3</sup> air h<sup>-1</sup> m<sup>-3</sup> digestate; and (c) 60 m<sup>3</sup> air h<sup>-1</sup> m<sup>-3</sup> digestate.

#### 4. Discussion

An experimental study was carried out on an ammonia stripping pilot plant, to investigate the influence of the main operating parameters on the ammonia removal efficiency.

A total of nine tests were carried out using a pilot bubble reactor stripping plant on digestate from anaerobic digesters treating a mixture of pig slurry and maize mash. The airflow rate, the temperature and the pH were identified as the main variables affecting the process. Tests were carried out varying the airflow rate from 30 to 60 m<sup>3</sup> air h<sup>-1</sup> m<sup>-3</sup> digestate.

and the temperature from 60 to 75 °C. In all tests, the pH increased from values between 8.2 and 9.1, up to over 10, in 2–4 h. The pH increased without the addition of basifying agents, which represents a relevant advantage, as discussed in Abbà et al. [18], for ammonia stripping. A recognized disadvantage of the ammonia stripping method is, in fact, the cost of alkali dosage. Ammonia stripping can be realized by the spontaneous increase of the pH due to the decomposition of alkalinity [16].

The ammonia removal yield increased with the increase in temperature and of airflow rate, with the temperature having a greater influence. Although these results were not directly comparable with those obtained in other works, e.g., due to the use of different stripping reactors, or operating conditions, they confirmed the parameters of influence on ammonia stripping highlighted in the literature. Previous studies on livestock manure [15,28] reported that high pH or high temperature led to high ammonia removal efficiencies. Zhao et al. found efficiencies higher than 90% at a temperature of 50–65 °C and pH 11, from screened anaerobically digested manure [28]. Guštin & Marinšek-Logar [25] found that ammonia removal efficiency of pig slurry centrate treated in a bench plant, in the range 30–70 °C and 20–120 m<sup>3</sup>/h, increased up to >90%.

Results of this experimental study permitted the construction of performance curves for ammonia removal to be used to determine the values of temperature, airflow and time, needed to obtain a certain performance. The ammonia removal rate, under tested conditions, could vary between 40% to 80%. As an example, 70% ammonia removal could be obtained by operating the system at a temperature of 65 °C in about 13 h with  $Q_{\text{air}} = 30 \text{ m}^3_{\text{air}} \text{ h}^{-1} \text{ m}^{-3}_{\text{digestate}}$ , as well as in about 10 h with  $Q_{\text{air}} = 45 \text{ m}^3_{\text{air}} \text{ h}^{-1} \text{ m}^{-3}_{\text{digestate}}$ , or in just over 8 h with  $Q_{\text{air}} = 60 \text{ m}^3_{\text{air}} \text{ h}^{-1} \text{ m}^{-3}_{\text{digestate}}$ . Similarly, the same performance (70% removal), could be achieved at a temperature of 60 °C, in about 19 h with  $Q_{\text{air}} = 30 \text{ m}^3_{\text{air}} \text{ h}^{-1} \text{ m}^{-3}_{\text{digestate}}$ , or in about 14 h with  $Q_{\text{air}} = 45 \text{ m}^3_{\text{air}} \text{ h}^{-1} \text{ m}^{-3}_{\text{digestate}}$ , or in 10.5 h with  $Q_{\text{air}} = 60 \text{ m}^3_{\text{air}} \text{ h}^{-1} \text{ m}^{-3}_{\text{digestate}}$ . Obtained results and performance curves are useful for farmers willing to reduce nitrogen content in digestates with similar characteristics to the tested one. Based on the heat available from the biogas from AD and the airflow rate to be used, the curves allow to establish the duration of the stripping process (and therefore the volume of reactor) to obtain the targeted ammonia removal yield. It is important to underline that presented results are strongly conditioned by the characteristic of the digestate, and of the pilot plant. Therefore, the results obtained cannot be generalized: testing other substrates, e.g., bovine digestate, may lead to different results and performances. Further experiments, carried out on different mixtures as input to the digesters, will be necessary to investigate how digestate characteristics influence the operation of the stripping plant.

The removal yields determined with the performance curves shown in Figure 5 refer only to the period when the process is stable and has reached the set temperature. During the temperature rise phase, an additional modest removal of ammonia occurs, which is not included in the model. The time required to reach stable conditions should also be added to the process time obtained from the model.

It is important to note that the pH rose spontaneously to around 10. Since the influence of this parameter on the ammonia removal efficiency is considerable, as demonstrated in the literature [15,23,25,27], this aspect should be taken into account, which limits the validity of the results obtained to the specific context of the experiment, especially with regard to the characteristics of the treated slurry.

In addition, it should be noted that, as the duration of the test increases, indicatively above 8 h, when operating at a temperature of 70 °C and an airflow rate of  $60 \text{ m}^3_{\text{air}} \text{ h}^{-1} \text{ m}^{-3}_{\text{digestate}}$ , problems related to excessive foaming may occur, with significant management consequences.

Finally, in the pilot plant used for the experimental study, the stripped ammonia was dispersed into the atmosphere, because the dimensions and scope of the plant focused on testing parameters rather than resource recovery. However, the ultimate aim of ammonia stripping, coupled with the reduction of the ammonia content in the diges-

tate for agricultural reuse, is the possibility of recovering the ammonia as a resource (i.e., ammonium sulphate) [29].

## 5. Conclusions

The experimental study confirmed the role of pH, temperature and airflow on ammonia removal efficiencies in a pilot air bubble reactor, with temperature having a greater influence than airflow. The ammonia removal efficiencies obtained reached values above 80%, at a temperature of 70 °C and an airflow of 45 and 60 m<sup>3</sup><sub>air</sub> h<sup>-1</sup> m<sup>-3</sup><sub>digestate</sub>. The pH increased spontaneously, without the addition of basifying agents, which allowed reduction in the costs of chemicals with respect other types of ammonia stripping technologies where reagents are required. The study led to the construction of performance curves, which are a simple and very effective tool to identify the operating conditions (temperature, airflow, time) required to obtain a predefined ammonia removal yield.

The results reported in this work refer to specific digestate used in the experimentation. Therefore, further research is needed to test digestates with different characteristics. Furthermore, the study was carried out in a pilot plant (though of significant size), and should be tested in a full-scale plant, where more severe conditions could also be investigated. The proposed experimental methodology could be replicated by other researchers to assess the effect of the operating parameters on the process performance, thus, in turn, promoting the use of air bubble stripping reactors and the recovery of ammonia and digestates as valuable resources.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/su151310494/s1>, Figure S1: Graphical elaborations of the temperature results in the tests.

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