

# Upgrading of biogas by utilizing aqueous ammonia and the alkaline effluent from air-stripping of anaerobically digested animal manure. Application on the design of a semi-industrial plant unit



D. Georgiou<sup>b,c,\*</sup>, V. Liliopoulos<sup>a,b</sup>, A. Aivasidis<sup>a</sup>

<sup>a</sup> Department of Environmental Engineering Democritus University of Thrace 67100 Xanthi, Greece

<sup>b</sup> Bioenercon Ltd73 Nikopoleos Str., Ioannina, 45221 Greece

<sup>c</sup> KETES (Hellenic Army Research & Technology Center) 211 Mesogion Avenue, Athens, 11525 Greece

## ARTICLE INFO

### Keywords:

Air-stripping  
Anaerobic digestion  
Animal manure  
Aqueous ammonia  
Biogas scrubbing  
Biomethane

## ABSTRACT

Biogas is acknowledged worldwide as an increasingly important renewable energy source. After treatment, the upgraded biogas (biomethane) can be injected into the existing natural gas infrastructure, or it can be compressed for usage as a vehicle fuel. Upgrading of biogas by chemical absorption is considered among the most attractive scrubbing technologies. There are disadvantages though when using alkylamines, such as the energy-intensive regeneration step, degradation of the amines and the potential to form harmful chemical compounds. However, the latter disadvantages could be overcome by using non-conventional methods. In our lab-scale experiments, aqueous ammonia derived from air-stripping of a lime-treated anaerobic digestate proved very effective as biogas scrubber, decreasing carbon dioxide substantially (over 90%), and removing hydrogen sulfide ( $H_2S$ ) completely. Moreover, the alkaline aqueous effluent of the latter air-stripping process was very effectively neutralized by the biogas, while it also exhibited an important scrubbing potential (removing  $CO_2$  and  $H_2S$  partially). Based upon the above experimental results, the flowsheets of an ammonia air-stripping/wet-scrubber and a biogas scrubbing unit, at a semi-industrial scale, were constructed and presented. Taking advantage of both the above acid gas chemical scrubbers could prove very beneficial for a cost-effective conversion of biogas to biomethane.

## 1. Introduction

Anaerobic digestion of animal manure offers great prospects for rural economic growth, gaining increasing popularity as a means to protect the environment and to recycle materials efficiently into the farming systems. Biogas is acknowledged worldwide as an important renewable energy source, producing mechanical power, heat and/or electricity. After treatment, upgraded biogas (biomethane) can be utilized in similar applications as natural gas, while it can also be compressed (200–250 bar) for usage as a vehicle fuel. Moreover, the utilization of biomethane counteracts the import dependency of natural gas and thus increases supply security [1–4].

Anaerobic digestate, as nutrient-rich slurry can be applied to agricultural land reducing thus the need for chemical fertilizers and pesticides. In many cases however, and because of its high ammonia content, the anaerobic digestate must be treated as a secondary waste effluent prior to its applications or to its disposal to the environment [5–7]. Ammonia, a highly reactive alkaline agent, neutralizes acidic

compounds in the atmosphere (e.g.  $SO_2$ ,  $NO_x$ ); forming ammonium aerosols which contribute to the well-known harmful effects on air quality and public health. Moreover, ammonia deposition on land and water causes eutrophication to water eco-systems, fish toxicity, and impacts on species diversity [8–11]. Thus, developing an integrated environmental management system for the reduction and recovery of ammonia from anaerobic digestate has become a very important issue the recent years [12–14]. *Air Stripping* has already been a successful process technique in order to remove ammonia from municipal and industrial wastewaters, landfill leachates and anaerobic digestates. *Air stripping* can be also combined with *acid absorption* in order to recover ammonia as nitrogen fertilizer, making this technique economically even more attractive [12,14–17]. Finally, the highly alkaline *Air-Stripping* aqueous effluent could be utilized in a chemical absorption process (e.g., packed-tower) in order to scrub carbon dioxide from biogas, contributing thus to the conversion of biogas to biomethane, while being neutralized in an environmentally friendly manner [12,18–20].

Conventional biogas upgrading methods can be categorized as

\* Corresponding author at: Odyssea Elyti 3, 13231 Petroupolis, Athens, Greece.

E-mail addresses: [dgeorgiou66@yahoo.com](mailto:dgeorgiou66@yahoo.com) (D. Georgiou), [v.liliopoulos@enerconpv.gr](mailto:v.liliopoulos@enerconpv.gr) (V. Liliopoulos), [spiadou@env.duth.gr](mailto:spiadou@env.duth.gr) (A. Aivasidis).

**Nomenclature**

AAP	Aqueous Ammonia Process
$COD_{Sol}$	Soluble Chemical Oxygen Demand ( $mg\ L^{-1}$ )
$COD_{Total}$	Total Chemical Oxygen Demand ( $mg\ L^{-1}$ )
EC	Electric Conductivity ( $mS\ cm^{-1}$ )
$H$	Henry constant for ammonia (dimensionless)
HRT	Hydraulic retention time (d)

OLR	Organic loading rate ( $g\ L^{-1}\ d^{-1}$ )
$Q_{air}$	Air flowrate ( $m^3\ h^{-1}$ )
$Q_{BG}$	Biogas flowrate ( $L\ d^{-1}$ )
$Q_L$	Anaerobic digestate flowrate ( $m^3\ h^{-1}$ )
PFR	Plug Flow Reactor
$T$	Temperature (Kelvin, or $^{\circ}C$ )
TS	Total solids ( $mg\ L^{-1}$ )
TSS	Total Suspended Solids ( $mg\ L^{-1}$ )

follows, scrubbing technologies (absorption methods), pressure swing adsorption (PSA), membrane separation and finally, cryogenic treatment which is only used in a few plants in Europe because of its high energy cost. Each of the methods mentioned has its advantages and disadvantages. The best choice of treatment technology should always be based on local conditions [21,22]. Scrubbing technology utilizing chemical absorption is among the most attractive ones due to its many advantages (low power requirement due to operation at ambient pressure, high loading of scrubbing liquid, high methane purity, low methane losses). However, there are also disadvantages when using alkylamine compounds (mono-ethanolamine, diethanolamine, N-methyldiethanolamine); the energy-intensive regeneration step (high heat requirement), the degradation of amines resulting in loss of raw material, and the potential to form harmful chemical species [23,24]. Nonetheless, the latter disadvantages could be overcome by utilizing non-conventional methods and different alkaline compounds (e.g. aqueous ammonia). Chemical absorption using the Aqueous Ammonia Process (AAP) has been recognized as a mature technology in the gas industry for treating acid gases such as  $CO_2$ ,  $SO_x$ , etc. [25–27].

In this respect, the objective of this preliminary study at lab-scale was to investigate the performance of aqueous ammonia as scrubbing agent for the upgrading of biogas (removing both  $CO_2$  and  $H_2S$ ). Moreover, ammonia was extracted from the same biogas-producing process (anaerobic digestion of animal manure) by air-stripping, rendering simultaneously the anaerobic digestate as environmentally friendlier for agricultural land applications. Furthermore, the alkaline aqueous effluent from the latter air-stripping process is neutralized in an environmentally friendly manner, while at the same time it also acts as a supplementary biogas scrubbing agent. Finally, the additional advantage of this process is that no energy-intensive regeneration step is required since ammonia is converted, at ambient conditions, to a useful end-product (fertilizer).

## 2. Materials and methods

### 2.1. Animal manure anaerobic digestion

Cow dung from a nearby farm was the main component (over 98% w/w) of the animal manure mixture utilized for anaerobic digestion. The rest of it consisted of glycerol (~ 1% w/w) and corn syrup (~ 1% w/w). A pilot-plant unit was utilized for the above animal manure anaerobic digestion under mesophilic conditions (36–38  $^{\circ}C$ ). For this purpose, a 50  $m^3$  continuous-mode Plug Flow Reactor (PFR) was employed. The feed flow-rate ( $Q_{Feed}$ ), the Organic Loading Rate (OLR), and the biogas production rate, as a mean value of the last two months of

operation (Dec. 2019–Jan. 2020), were  $6.35 \pm 2.42\ m^3/d$ ,  $11.06 \pm 4.3\ kg\ COD/(m^3\ d)$ , and  $118.76 \pm 56.25\ m^3/d$ , respectively. The physico-chemical characteristics of the animal manure mixture and the corresponding anaerobic digestate as well as biogas composition, for the last two months of operation (Dec. 2019–Jan 2020), are given in Table 1.

### 2.2. Lime treatment – solids settling

Commercial “hydrated lime” ( $Ca(OH)_2$ ) in the form of a 50%-solids slurry was utilized to raise the pH of the anaerobic digestate and to precipitate the solids (as a coagulation/flocculation agent). An elevated pH value of  $12.0 \pm 0.1$  was chosen for improved clarification of the anaerobic digestate and effective ammonia air-stripping. After sedimentation, the solids were separated and the supernatant liquid was filtrated by a common filter. Details about the exact experimental procedure can be found elsewhere [12,28].

### 2.3. Air-stripping of ammonia followed by water-absorption

#### 2.3.1. Materials

Ammonia air-stripping took place in a packed-tower installation which consisted of a water-jacketed glass column of a height of 1.35 m and an internal diameter of 8 cm. Glass-made cylinders of the “Raschig Ring” type, of a size of 1 cm and a thickness of 2 mm were utilized as the packing material; the packing bed had a total height of 0.95 m. Temperature was maintained constant at  $45 \pm 1\ ^{\circ}C$  by means of a water-bath and an external water-coil. The water-bath was also connected to a heat-exchanger in order to pre-heat the wastewater influent prior to its entrance into the packed tower. An electric blower (Hiblow HP-120) and a peristaltic pump (Watson-Marlow 501U) were utilized for air supply (~ 3180  $L\ h^{-1}$ , standard value by the manufacturer) and wastewater inflow (1.0–13  $L\ h^{-1}$ ), respectively. The end of the wastewater inlet pipe was connected to a hole-tube for a better distribution of the wastewater on the packing material. The aqueous effluent was collected from the bottom of the packed-tower manually (using a control-valve). Finally, lime-treated anaerobic digestate was utilized as the inflow aqueous solution for the experiments. In order to obtain an air-flow of the highest possible in practice ammonia content (corresponding to around 6.0–6.5 g/L of ammonium in the anaerobic digestate), the latter anaerobic digestate was enriched by adding ammonium chloride.

The ammonia-rich air-flow from the exit (top) of the air-stripper was divided into two air-flow lines. The first line was guided into the atmosphere and the second one into the water-scrubber installation (at the bottom of the packed-bed), after it had been cooled down to around

**Table 1**

Animal manure mixture and anaerobic digestate physicochemical characteristics-biogas composition and yield (mean values of two months of operation).

	pH	$COD_{Total}$ (g/L)	EC (mS/cm)	TSS (g/L)	TS (g/L)	N-NH <sub>4</sub> <sup>+</sup> (g/L)
Animal manure mixture	$7.3 \pm 0.1$	$54.5 \pm 5.5$	$13.1 \pm 1.1$	$24.1 \pm 1.6$	$34.32 \pm 5.1$	–
Anaerobic digestate	$7.5 \pm 0.1$	$8.8 \pm 0.6$	$15.4 \pm 0.7$	$23.5 \pm 2.1$	–	$1.04 \pm 0.2$
Biogas composition:	$CH_4$ (%): $66.1 \pm 1.6$ , $CO_2$ (%): $34.5 \pm 1.5$ , $H_2S$ (ppm): $801.3 \pm 552.0$					
Biogas yield ( $m^3/kg\ COD$ ):	$0.22 \pm 0.04$					

$COD_{Total}$ : Total Chemical Oxygen demand; EC: Electric Conductivity; TSS: Total Suspended Solids; TS: Total Solids.

$20 \pm 1$  °C by a water-glass-coiled-reflux condenser. Prior to entering the scrubber, the volumetric air-flow was regulated by means of air-flow rotameters at  $150$  to  $1500$  L h<sup>-1</sup>. The wet-scrubber (packed-tower) consisted of a glass column of a total height of  $70$  cm and an internal diameter of  $5$  cm. Constant recirculation of the aqueous ammonia solution (at  $0.5$ – $1.0$  L min<sup>-1</sup>) counter-currently contacting the air, was provided using a water pump. The above-described packing material ("Raschig Ring") was also utilized, while the packed-bed height was equal to  $20$  cm. Deionized water was utilized to keep the pH of the recirculating aqueous ammonia solution at the desired value (pH =  $11.5$ – $11.8$ ), by means of a pH-regulator and a small peristaltic pump. Aqueous ammonia solutions at increasing concentrations ( $1.5$ – $5\%$  w/v) were collected from the bottom of the packed tower manually (using a control-valve), in order to be utilized for the biogas scrubbing experiments. The latter aqueous ammonia solutions were obtained by fixing the value of the pH-regulator at the proper level. Finally, ammonia concentration in the air-flow was determined using the special Ammonia Dräger tubes (made in Germany). The flowsheet and a photo of the air-stripper/wet-scrubber installation are presented in Fig. 1.

### 2.3.2. Experimental procedure

Lime-treated anaerobic digestate was initially introduced into the air-stripper while the temperature was regulated at the desired level ( $45 \pm 1$  °C). After initiating the air flow into the stripper at a gas to liquid ratio ( $Q_{air}/Q_L$ ) equal to  $2000$ , and after stabilization of the

operating temperature, the system was left to operate for  $15$  min before taking air and aqueous effluent samples (a time-period that was more than enough for the system to reach steady-state conditions). Aqueous effluent from the bottom of the air-stripper was collected in order to be used for biogas scrubbing.

Stripping factor ( $S$ ) comprises one of the most important parameters of air-stripping process (Eq. (1)) [29].

$$S = \frac{Q_{air}}{Q_L} H \quad (1)$$

where,  $H$ : Henry constant for ammonia (dimensionless); a function of temperature ( $T$ , Kelvin) given by Eq. (2) [30]:

$$H = 0.0006e^{\left[4340\left(\frac{1}{293} - \frac{1}{T}\right)\right]} \quad (2)$$

In practice, the stripping factor is usually regulated in the range:  $S = 3$ – $5$  [14,29]. Hence, a  $G/L$  ratio equal to  $2000$  (as in our case) gives a very satisfactory value to the stripping factor, as derived by Eqs. (1) and (2) ( $S = 3.84$  for  $T = 45$  °C).

Part of the ammonia-rich air flow from the above air-stripping process and after it had been cooled down to  $20 \pm 1$  °C, was directed to the bottom of the scrubber's packing bed at  $1500$  L h<sup>-1</sup> till the pH of the recirculating water in the scrubber reached the value of  $10 \pm 0.1$  (corresponding to an aqueous ammonia concentration of  $\sim 0.001\%$  w/v). The pH was thereafter kept constant by means of the pH-regulator and deionized water. The experimental run continued by investigating

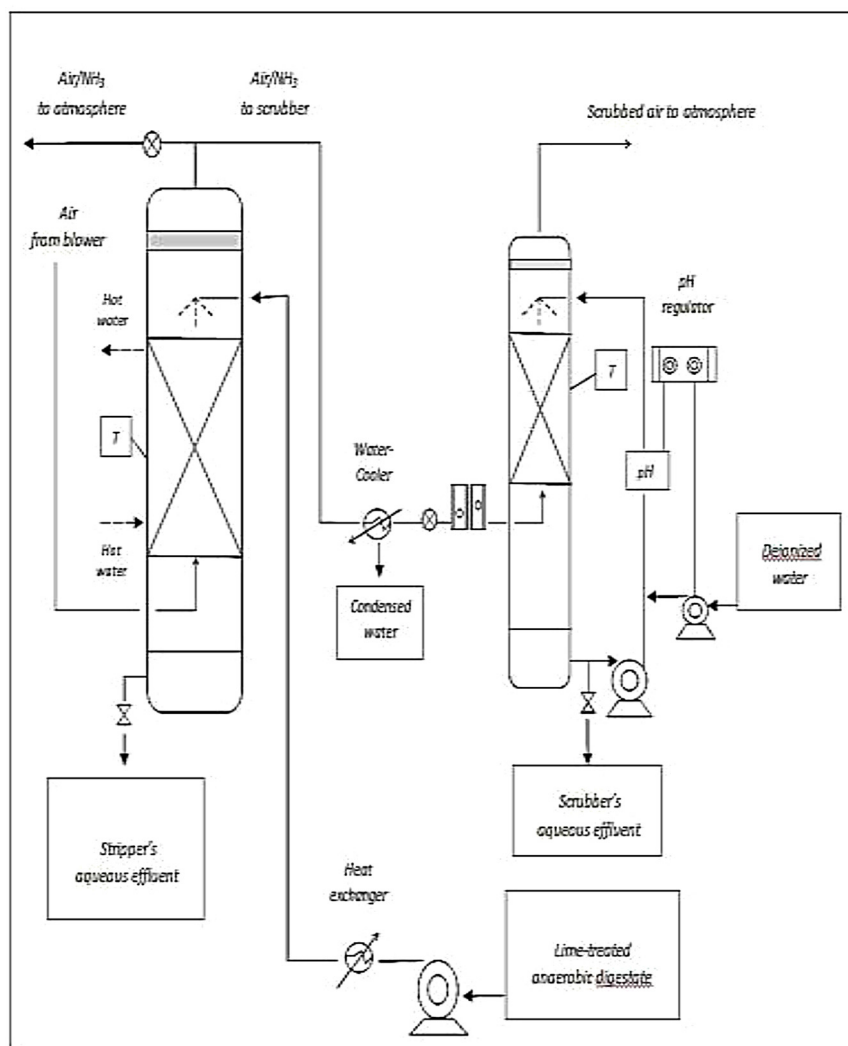


Fig. 1. Flowsheet and a photo of the ammonia air-stripper/wet-scrubber installation.

ammonia absorption in the scrubber under constant pH ( $10 \pm 0.1$ ). Air samples from the top of the scrubber were analyzed for ammonia concentration at several volumetric air-flow values (10 min of continuous operation at the desired volumetric air-flow value was more than enough for the system to reach steady-state conditions). The pH of the recirculating aqueous ammonia solution was then fixed at increasing values (pH = 11.5–11.8) and the system was operated at high air-flow (1500 L h<sup>-1</sup>), until adequate amounts of concentrated aqueous ammonia solutions were collected (1.5 and 5% w/v). Highly concentrated aqueous ammonia (25% w/w) was also added in the recirculating solution for faster production of the latter ammonia solutions (due to low air-flow rate). Finally, absorption of gaseous ammonia was once more investigated at a high aqueous ammonia concentration this time (5% w/v).

It's been well established that during the absorption process gas film resistance controls for highly soluble gases [31]. Ammonia as indeed a highly soluble gas has its main resistance in the gas phase. Taking into account the above fact and assuming steady state conditions, as well as

ammonia being an ideal gas, the following simplified equation can be applied for the calculation of ammonia's overall mass transfer coefficient ( $K_G \alpha$ , Eq. (3)), after solving the respective mass balance equation. This is a case of a fast reaction in liquid film with high reactant concentration (dissolved gaseous ammonia reacting with water) [31].

$$K_G \alpha = \frac{Q_{air}}{RTSZ} \left( \ln \frac{y_{NH_3, in}}{y_{NH_3, out}} \right) \quad (3)$$

where,  $K_G \alpha$  = Overall mass transfer coefficient for ammonia (kmol m<sup>-3</sup> h<sup>-1</sup> atm<sup>-1</sup>)

$Q_{air}$  = Air flow-rate (m<sup>3</sup> h<sup>-1</sup>)

$R$  = Universal gas constant ( $R = 0.08206 \text{ m}^3 \text{ atm K}^{-1} \text{ kmol}^{-1}$ )

$T$  = Temperature (Kelvin)

$S$  = packed-tower cross-sectional area (m<sup>2</sup>);  $S = \pi D^2/4$  ( $D$  = packed-tower internal diameter, m)

$Z$  = Packed-bed height (m)

$y_{NH_3, in}$  = molar mass fraction of ammonia in air (scrubber inlet),

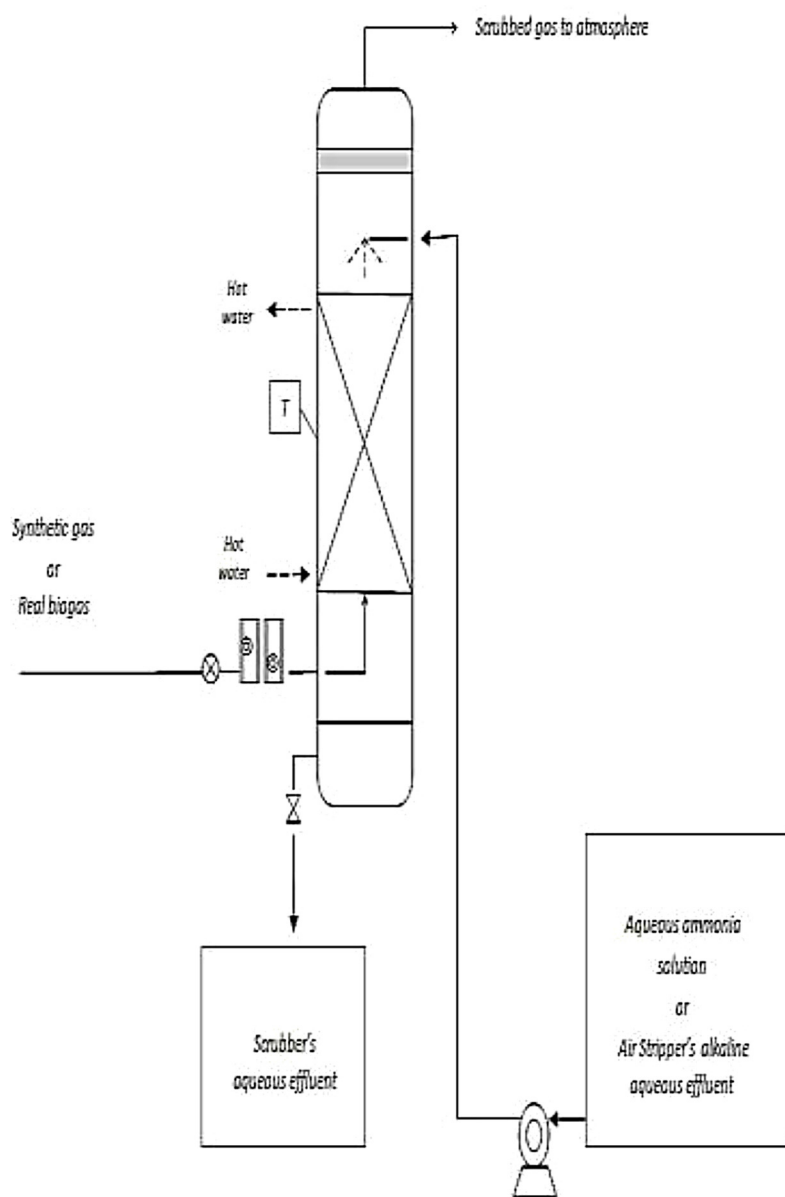
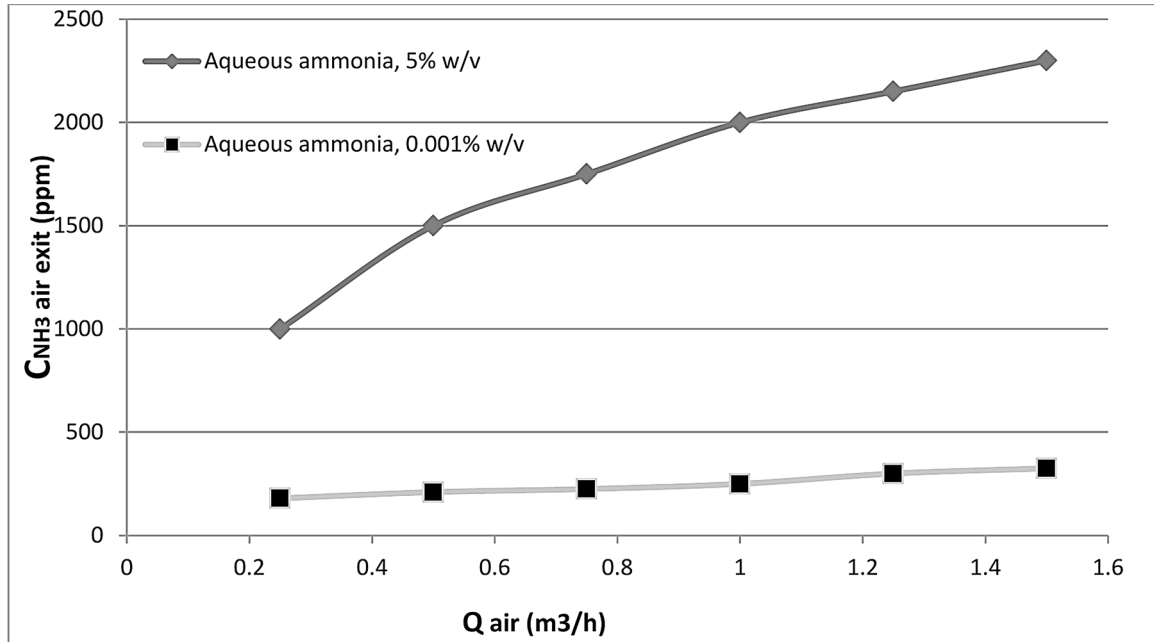


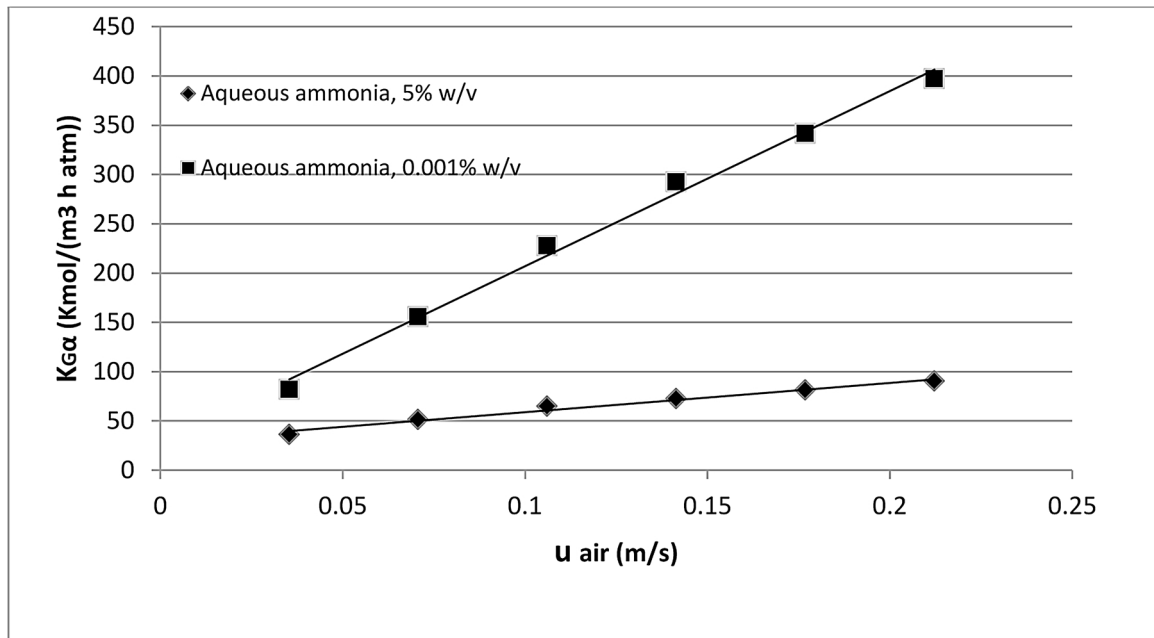
Fig. 2. Flowsheet and a photo of the biogas wet-scrubber set-up.

ppm  
 $y_{NH_3, out}$  = molar mass fraction of ammonia in air (scrubber exit),  
 ppm

After having determined experimentally the  $K_G\alpha$  coefficient values for ammonia, the respective height (Z) of the packed-bed that is necessary for complete ammonia capture (e.g. ammonia



(a)



(b)

$$K_G\alpha = 1610.02u_{air}^{0.885}, R^2 = 0.998 - (NH_{3(aq)} : 0.001\%w/v)$$

$$K_G\alpha = 196.76u_{air}^{0.505}, R^2 = 0.998 - (NH_{3(aq)} : 5\%w/v)$$

**Fig. 3.** Ammonia scrubbing data; (a) ammonia concentration in air exit vs. air-flow ( $Q_{air}$ ), (b)  $K_G\alpha$  vs. superficial air velocity ( $u_{air}$ ).  
 $C_{NH_3, air-in}$ : Air-ammonia concentration, in ( $4000 \pm 100$  ppm);  $Q_{air}$ : Volumetric air flow ( $m^3 h^{-1}$ );  $u_{air}$ : superficial air velocity ( $m s^{-1}$ );  $C_{NH_3, air-exit}$ : Air-ammonia concentration, exit (ppm);  $K_G\alpha$ : Overall mass transfer coefficient for ammonia ( $kmol m^{-3} h^{-1} atm^{-1}$ )



concentration < 5 ppm), can be calculated by Eq. (4) (as derived by Eq. (3)).

$$Z = \frac{Q_{air}}{RTSK_G\alpha} \left( \ln \frac{y_{NH_3,in}}{y_{NH_3,out}} \right) \quad (4)$$

## 2.4. Scrubbing of biogas by CO<sub>2</sub> and H<sub>2</sub>S chemical absorption

### 2.4.1. Materials

The above-described air-stripper installation (Fig. 1) was converted to a wet scrubber set-up. Temperature was maintained constant at  $25 \pm 1$  °C this time by means of the water-bath and the external water-coil. The aqueous ammonia solutions (1.5 and 5% w/v), and the alkaline aqueous effluent from air-stripping of the lime-treated anaerobic digestate, counter-currently contacted the gas phase and were then collected from the bottom of the packed tower. Synthetic gas (80% N<sub>2</sub> – 20% CO<sub>2</sub>) as well as real biogas from the anaerobic digestion pilot-plant (PFR) were utilized for the study. A pressure-regulator and air-flow rotameters were employed to inject the synthetic gas into the wet scrubber set-up at the desired volumetric air-flow, while the scrubbed gas was then rejected into the atmosphere. Moreover, real biogas was collected in special 400 L bags; an air-pump was employed in order to inject the biogas into the wet scrubber, at a flow rate of 1000 L h<sup>-1</sup>. The flowsheet of the wet scrubber set-up is presented in Fig. 2.

### 2.4.2. Experimental procedure

The alkaline aqueous effluent from air-stripping of the lime-treated anaerobic digestate was initially introduced into the wet scrubber installation, at a constant flowrate ( $\sim 12.3$  L h<sup>-1</sup>). The synthetic gas was then injected into the above scrubber installation at different volumetric flow rates (150 to 1500 L h<sup>-1</sup>). At each volumetric gas flow rate, the system was left to run for at least 10 min; air-samples were then collected from the exit (top) of the wet scrubber in order to be analyzed for carbon dioxide concentration using a biogas analyzer (Gas Data GFM435, made in UK). Samples from the aqueous effluent were also selected (from the bottom of the wet scrubber), and their pH was

recorded. The above experiments were then repeated using this time real biogas at constant volumetric air-flow (1000 L h<sup>-1</sup>). Apart from carbon dioxide, hydrogen sulfide (H<sub>2</sub>S) concentration was also determined in the air-samples by the above-mentioned biogas analyzer (Gas Data GFM435).

Finally, the synthetic and real biogas scrubbing experiments were repeated utilizing this time the aqueous ammonia solutions (1.5 and 5% w/v). The extent of total ammonia slip was also reported in the latter experiments by analyzing the ammonia concentration in the air exit (using the special Ammonia Dräger tubes).

## 2.5. Wastewater analytical methods

APHA Standard Methods [32] were utilized for wastewater (raw and treated anaerobic digestate) physicochemical analysis. Total alkalinity was measured by titration with standardized sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) solution using end-point indicator (methyl-orange) and/or a pH-meter (Hanna HI 83141). COD was calculated using a COD-digestion unit (VELP Scientifica) according to the Open Reflux Method; titration with ferrous ammonium sulphate was preferred over photometric analysis [32].

## 3. Results and discussion

### 3.1. Air-stripping of ammonia followed by water-absorption

Air-stripping of the lime-treated anaerobic digestate resulted in the production of an ammonia-rich air-flow with a concentration of  $4000 \pm 100$  ppm (ammonia in the air was measured 4 times during the course of the experiment giving a constant value). Moreover, the air-stripping aqueous effluent was almost totally depleted of ammonia (over 99%). Absorption of ammonia in the wet-scrubber by deionized water was then investigated at a continuous mode and at ambient conditions ( $P = 1$  atm,  $T = 20 \pm 1$  °C). Furthermore, the latter absorption process was investigated at a low and a high aqueous ammonia concentration (0.001% and 5% w/v, respectively). Although the

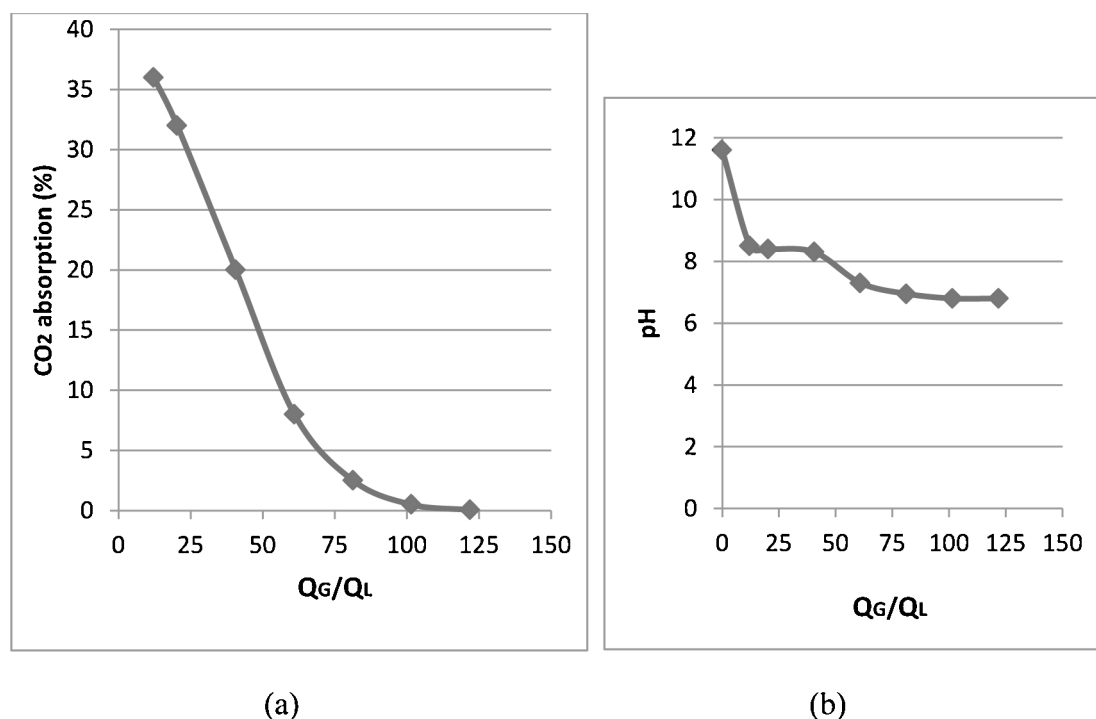


Fig. 4. (a) Carbon dioxide absorption (%) and (b) Aqueous effluent pH vs. (Q<sub>G</sub>/Q<sub>L</sub>) ratio (Lime-treated anaerobic digestate). Q<sub>G</sub> = Synthetic gas flow-rate (L h<sup>-1</sup>); Q<sub>L</sub> = Aqueous effluent flow-rate (12.3 L h<sup>-1</sup>).

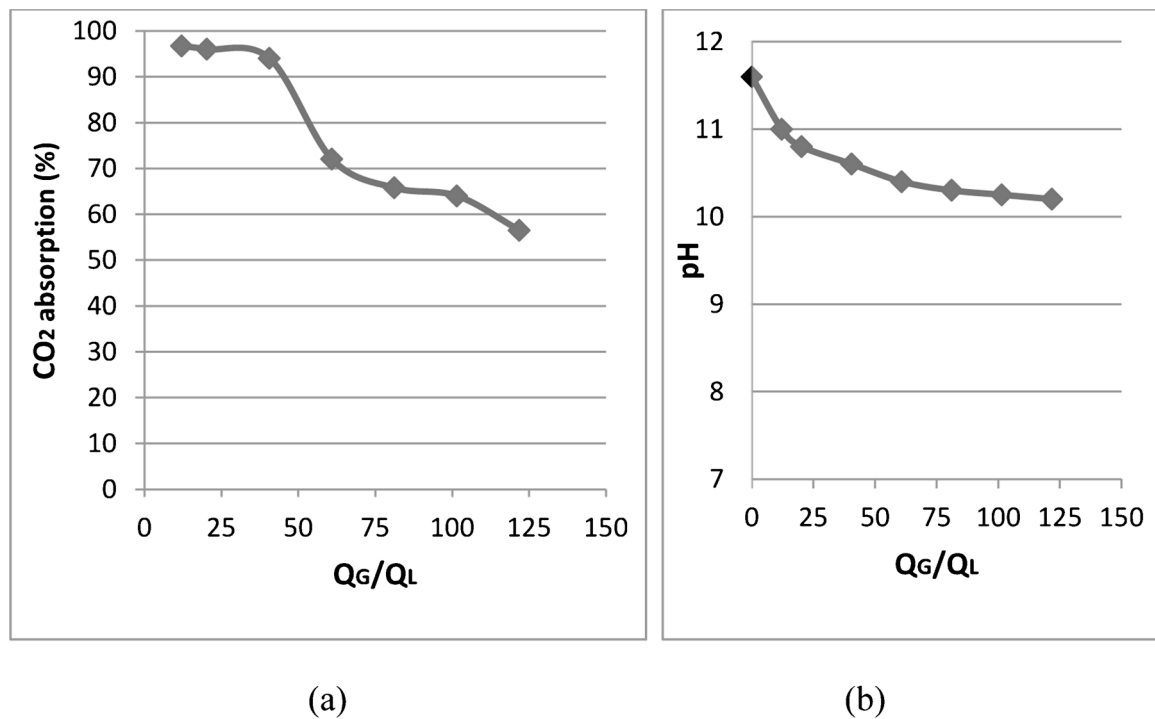


Fig. 5. (a) Carbon dioxide absorption (%) and (b) Aqueous effluent pH vs. ( $Q_G/Q_L$ ) ratio (Aqueous ammonia solution, 1.5% w/v).  $Q_G$  = Synthetic gas flow-rate ( $L h^{-1}$ );  $Q_L$  = Aqueous effluent flow-rate ( $12.3 L h^{-1}$ ).

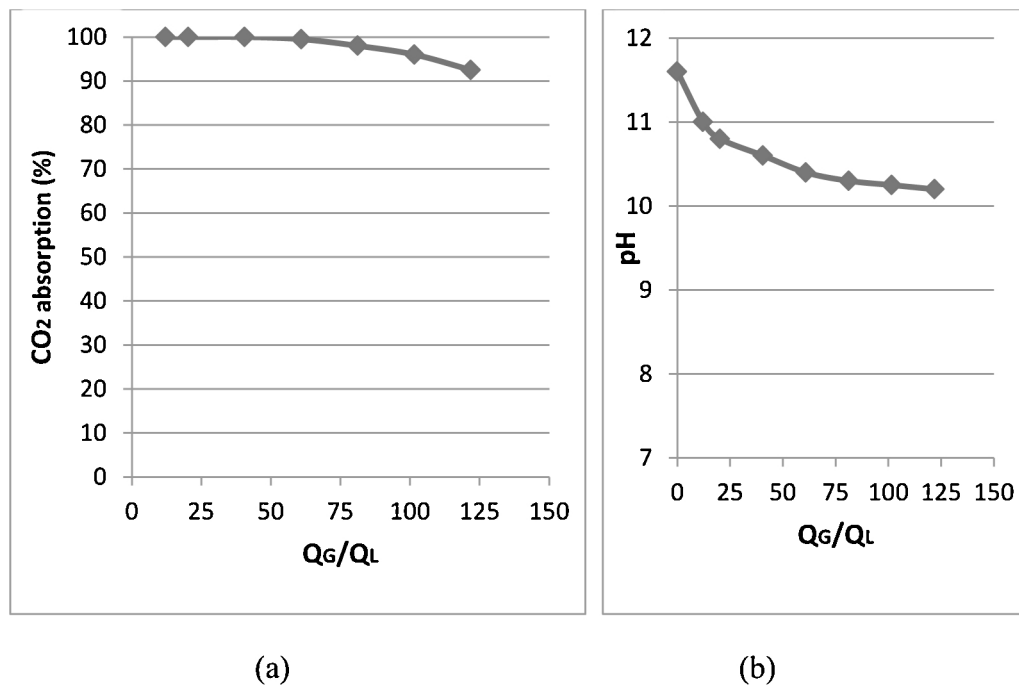


Fig. 6. (a) Carbon dioxide absorption (%) and (b) Aqueous effluent pH vs. ( $Q_G/Q_L$ ) ratio (Aqueous ammonia solution, 5% w/v).  $Q_G$  = Synthetic gas flow-rate ( $L h^{-1}$ );  $Q_L$  = Aqueous effluent flow-rate ( $12.3 L h^{-1}$ ).

packed-bed height was relatively small (20 cm), high absorption efficiency was demonstrated by the scrubber set-up, as shown in Fig. 3a (over 90% in the diluted aqueous ammonia solution, and 42–75% in the concentrated one for all volumetric air-flow rates). Incorporating all the respective experimental data in Eq. (3), ammonia overall mass transfer coefficient ( $K_G a$ ) was calculated at several volumetric air-flow values, for the two different aqueous ammonia concentrations (Fig. 3b). As expected,  $K_G a$  increased substantially by increasing the volumetric air-

flow rate. Moreover,  $K_G a$  was approximated as a function of superficial air velocity with a high degree of accuracy (Fig. 3b). The  $K_G a$  coefficient varied with air velocity to the  $n$ -power where  $n$  ranged from 0.505 to 0.885. This range is close enough to the exponents reported in literature [33–36]. As also expected, performing the experiment at a high aqueous ammonia concentration (5% w/v as opposed to 0.001% w/v), resulted in much lower  $K_G a$  values due to substantial decrease of the ammonia mass transfer driving force. Hence, at 5% w/v, the

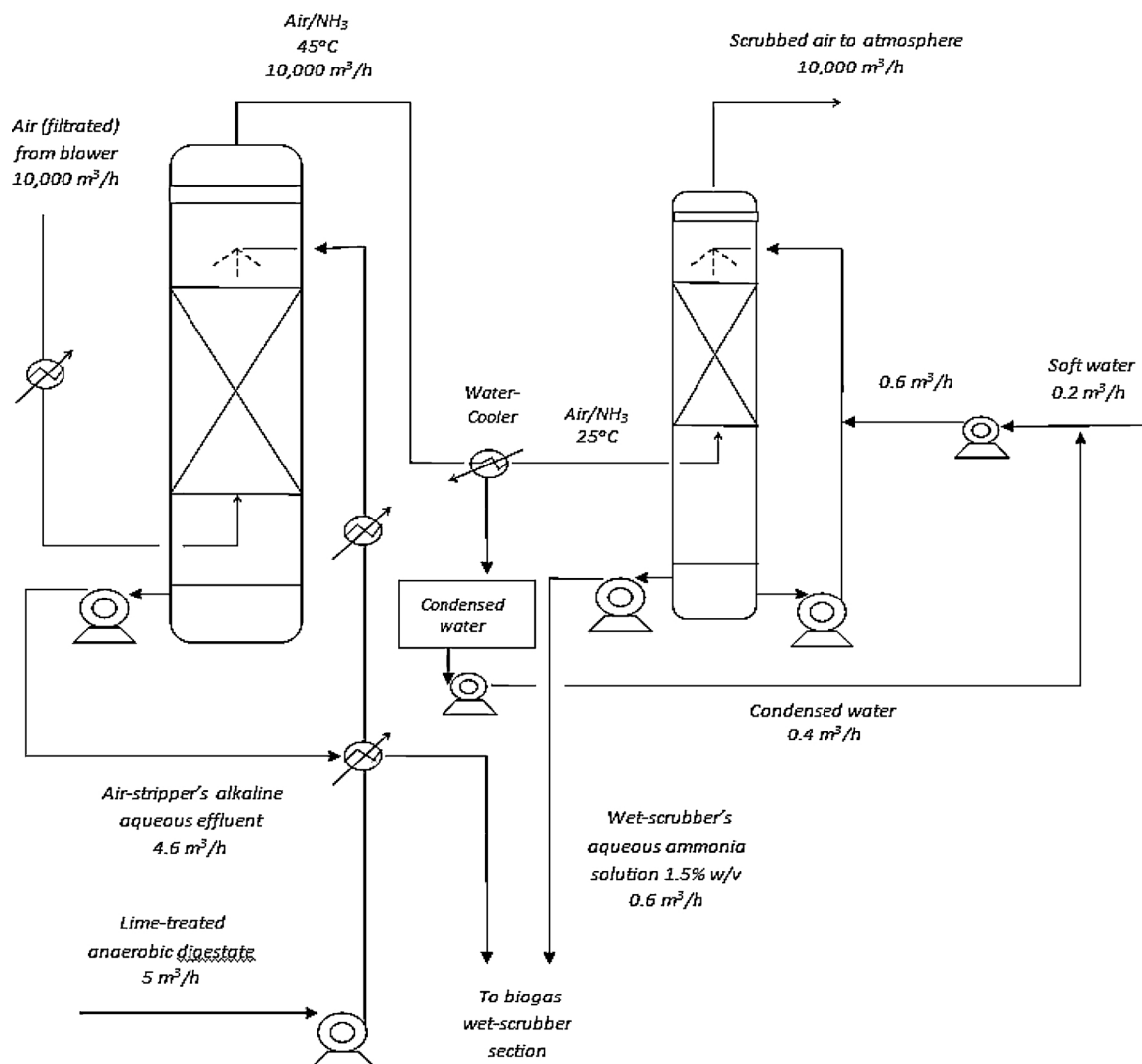


Fig. 7. Flowsheet of the semi-industrial ammonia air-stripper/wet-scrubber unit.

concentration of dissolved gaseous ammonia in the aqueous phase became important and so did liquid bulk resistance, leading so to reduced  $K_G a$  values [31].

From Eq. (4), and for an air flow-rate ( $Q_{air}$ ) of  $1500 \text{ L h}^{-1}$ , the packed-bed height of the wet-scrubber (Fig. 1) for almost complete ammonia capture (e.g. 5 ppm of ammonia in air-exit) is equal to 0.53 m and 2.35 m, for aqueous ammonia solution of 0.001% w/v (pH =  $10.0 \pm 0.1$ ) and 5% w/v (pH =  $11.6 \pm 0.1$ ), respectively.

Taking into consideration the above experimental results, it is evident that extracting ammonia from lime-treated anaerobic digestate and producing an aqueous ammonia solution of the desired concentration is indeed technically feasible. The total volumetric flow of the latter solution depends entirely upon the volumetric flow of the anaerobic digestate, its respective ammonia concentration and the concentration of the final aqueous ammonia solution. The latter experimental data will be used for the design of a semi-industrial air-stripper/wet-scrubber installation, targeting at total ammonia capture and at the production of an aqueous ammonia solution that will be used for the upgrading of biogas (3.4 Semi-industrial plant operation design).

### 3.2. Air-stripping aqueous effluent neutralization by $\text{CO}_2$ absorption

Synthetic gas (80%  $\text{N}_2$  – 20%  $\text{CO}_2$ ) was initially used, at increasing volumetric flow-rate, in order to study  $\text{CO}_2$  absorption and the respective neutralization of the alkaline aqueous effluent from air-

stripping of the lime-treated anaerobic digestate. As demonstrated in Fig. 4, the latter air-stripping aqueous effluent can be neutralized (pH =  $8.5 \pm 0.1$ ) even at the minimum synthetic gas flow-rate. Concurrently and as expected, absorption of  $\text{CO}_2$  reaches its maximum efficiency (36%). Increasing synthetic gas flow-rate results in the decreasing of  $\text{CO}_2$  absorption, while the pH of the aqueous effluent reaches its minimum possible value (pH =  $6.8 \pm 0.1$ ).

Real biogas (62%  $\text{CH}_4$  – 38%  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ : 1880 ppm) was also pumped into the wet-scrubber, at a flow-rate of  $1000 \text{ L h}^{-1}$ , resulting in total neutralization of the aqueous effluent (pH =  $6.8 \pm 0.1$ ). As in the above case (synthetic gas), carbon dioxide absorption rate was only minor (less than 0.5%). However, the concentration of hydrogen sulphide ( $\text{H}_2\text{S}$ ) was drastically reduced ( $< 100 \text{ ppm}$ ). Neutralization of the ammonia air-stripping aqueous effluent by real biogas seems indeed to be a very cost-effective and environmentally friendly technique.

### 3.3. Absorption of $\text{CO}_2$ in aqueous ammonia solutions (biogas scrubbing)

The aqueous ammonia solution of 1.5% w/v was initially utilized in order to scrub the synthetic gas. Fig. 5a presents the results of carbon dioxide absorption at an increasing gas-to-liquid volumetric flow-rate ratio, while the drop of the aqueous effluent pH is respectively demonstrated in Fig. 5b. Less than 1% of carbon dioxide remained in the synthetic gas at a low gas flow-rate ( $150 \text{ L h}^{-1}$ ) while, an absorption efficiency of more than 50% was depicted at the highest gas flow-rate



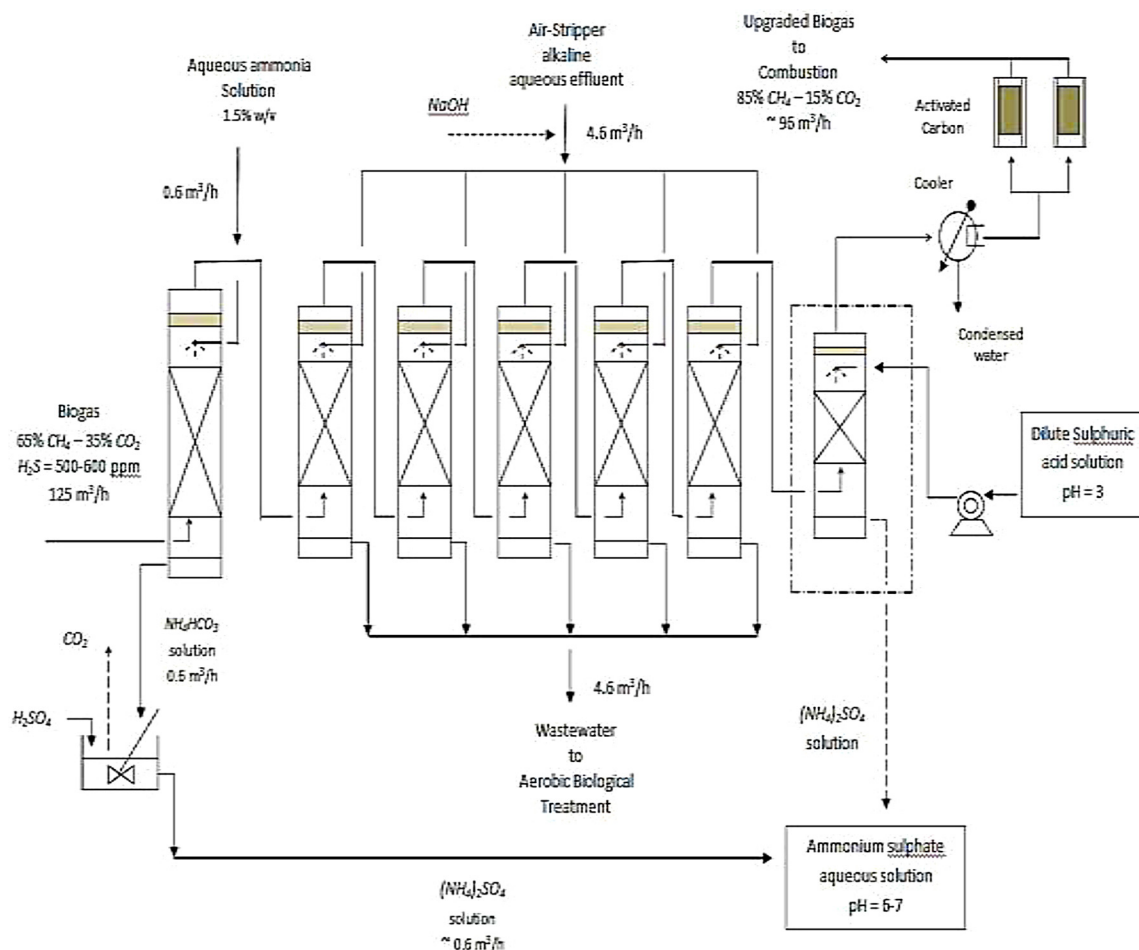


Fig. 8. Flowsheet of the semi-industrial biogas wet-scrubber unit.

(1500 L h<sup>-1</sup>). From Fig. 5b it is evident that the remaining alkaline aqueous effluent (with a pH > 9.5 even at the highest gas flow-rate) has the potential of greater absorption efficiency (e.g. by increasing the packed-bed height). Finally, an ammonia slip of 150–500 ppm was recorded by increasing gas flow-rate from 150 to 1500 L h<sup>-1</sup>, respectively.

Real biogas (62% CH<sub>4</sub> – 38% CO<sub>2</sub>, H<sub>2</sub>S: 1880 ppm) was then introduced into the wet-scrubber at a flow-rate of 1000 L h<sup>-1</sup>. Upgraded biogas exited the wet-scrubber having a composition of 86% CH<sub>4</sub> – 14% CO<sub>2</sub>, while the pH of the aqueous effluent dropped down to the value of 9.70. The latter results come in straight accordance with the above synthetic gas experiment (Fig. 5). Furthermore, hydrogen sulphide was completely removed.

All the above experiments were then repeated using this time the 5% w/v aqueous ammonia solution. Almost complete carbon dioxide absorption was observed at all gas-to-liquid volumetric flow-rate ratios utilizing the synthetic gas (Fig. 6a), while the pH of the aqueous effluent remained high at all times (pH > 10.20, Fig. 6b). Moreover, real biogas was entirely converted to biomethane (99% CH<sub>4</sub> – 1% CO<sub>2</sub>) with also total removal of hydrogen sulphide. However, a higher amount of gaseous ammonia escaped this time from the exit of the wet-scrubber (from 2500 ppm at low gas flow-rate to 10,000 ppm at the highest flow-rate).

### 3.4. Semi-industrial plant operation design

Apart from the 50 kW pilot-plant (PFR) that has been already under operation for about a year now, a 250 kW semi-industrial plant is currently under construction in the local industrial area (Xanthi,

Greece). The latter semi-industrial plant is also targeting at the production of biogas by the anaerobic digestion of animal manure mixtures in a 350 m<sup>3</sup> Plug Flow Reactor. Based upon the above experimental results, a simulation of the real operational conditions of ammonia air-stripper/wet-scrubber and biogas wet-scrubber units is given in the flowsheets of Fig. 7 and Fig. 8.

The construction of the above flowsheets is based on the following parameters:

- Anaerobic digestate flow-rate (QL): 120 m<sup>3</sup> d<sup>-1</sup> (5 m<sup>3</sup> h<sup>-1</sup>)
- Biogas flow-rate (QBG): 3000 m<sup>3</sup> d<sup>-1</sup> (125 m<sup>3</sup> h<sup>-1</sup>)
- Ammonia concentration in anaerobic digestate: 2 g L<sup>-1</sup>
- Air-Stripper operational temperature: 45 °C
- Air to liquid (anaerobic digestate) volumetric flow-rate ratio (Qair/QL): 2000
- Ammonia Air-Stripping efficiency: 90%
- Ammonia Wet-Scrubber operational temperature: 25 °C
- Ammonia capture in Wet-Scrubber: 100%
- Biogas Wet-Scrubber unit operational conditions: Ambient

Ammonia concentration varies depending on the type of animal manure mixture. The above value (2 g L<sup>-1</sup>) was chosen as future average concentration in the anaerobic digestate. Condensed water from cooling the hot air-stripping flow comprises roughly 2/3 of the water amount needed for the production of the aqueous ammonia solution. Therefore, condensed water is designed to be recycled (Fig. 7).

The 1.5% w/v aqueous ammonia solution was preferred due to less ammonia slip problems. The air-stripping alkaline aqueous effluent is expected to capture ammonia entirely from biogas, in the respective

wet-scrubber unit (Fig. 8). However, and for safety reasons, an acid scrubber (utilizing dilute sulphuric acid) was added in the end of the wet-scrubbing line ensuring total ammonia capture. In order to maximize scrubbing efficiency and to avoid flooding problems, the air-stripping aqueous effluent was split into 5 equal flowrate-lines, one for each wet-scrubber. The biogas, after passing through all the wet-scrubber towers, is then dehydrated in a cooling system. Finally, it passes through an activated carbon column before combustion (Fig. 8). Furthermore, experiments proved that by adding ferrous sulphate in the animal manure mixture (500 mg/kg COD) before the anaerobic digestion, hydrogen sulphide ( $H_2S$ ) concentration in biogas can be kept at a low level (500–600 ppm). According to our lab experimental results, the upgraded biogas is expected to reach a composition of at least 85%  $CH_4$  – 15%  $CO_2$ , and to be clear of hydrogen sulphide. Adding minor quantities of caustic soda solution in the air-stripping aqueous effluent would ensure the above expected results (Fig. 8).

Ammonium bicarbonate aqueous solution is produced in the first wet-scrubber where aqueous ammonia reacts with carbon dioxide. Due to the unstable nature of the latter chemical compound and the possible threat to the environment (this chemical is considered hazardous by the 2012 OSHA Hazard Communication Standard (29 CFR 1910.1200)) [37], a decision was made to convert it to the more stable and environmentally safe, ammonium sulphate solution (reacting with sulphuric acid solution in an open to atmosphere fast-stirring tank) (Fig. 8).

Presenting the technical details of the latter flowsheets (Fig. 7 and 8) would be out of the scope of this paper. Full description of the 250 kW semi-industrial plant operation will be given in a future publication.

#### 4. Conclusions

Aqueous ammonia solutions (1.5% and 5% w/v) were produced from air-stripping of a lime-treated anaerobic digestate (from the anaerobic digestion of animal manure), utilizing pure (deionized) water as the scrubbing agent. The latter aqueous ammonia solutions proved very effective acting as biogas scrubbers, absorbing carbon dioxide substantially (over 90%) while removing hydrogen sulphide completely.

The alkaline aqueous effluent of the air-stripping process was neutralized by the biogas in a cost-effective and an environmentally friendly manner. The latter air-stripping aqueous effluent can also be utilized as a supplementary scrubbing agent, removing  $CO_2$  and  $H_2S$  partially, while it can also capture ammonia that escapes from the first wet-scrubber stage.

Based upon the experimental data, the flowsheets of ammonia air-stripping/wet-scrubber and biogas scrubbing unit, at a semi-industrial scale, were constructed and presented.

#### Declaration of Competing Interest

None.

#### Acknowledgements

This research has been co-financed by the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE (project code:T1EDK-00471).

#### References

- [1] M.A. Eyl-Mazzega, C. Mathieu, Biogas and Biomethane in Europe: Lessons From Denmark, Germany and Italy, *Études de l'Ifri*, Ifri, Paris, France, 2019 [https://www.ifri.org/sites/default/files/atoms/files/mathieu\\_eyl-mazzega\\_biomethane\\_2019.pdf](https://www.ifri.org/sites/default/files/atoms/files/mathieu_eyl-mazzega_biomethane_2019.pdf).
- [2] N. Scarlat, F. Fahl, J.F. Dallemand, F. Monforti, V.A. Motola, Spatial analysis of biogas potential from manure in Europe, *Renew Sust Energ Rev* 94 (2018) 915–930.
- [3] C. Cowley, W. Brorsen, Anaerobic digester production and cost functions, *Ecol. Econ.* 152 (2018) 347–357.
- [4] B. Blumenstein, T. Siegmeier, D. Möller, Economics of anaerobic digestion in organic agriculture: between system constraints and policy regulations, *Biomass Bioenerg* 86 (2016) 105–119.
- [5] L. Evans, A.C. VanderZaag, V. Sokolov, H. Balde, D. MacDonald, C. Wagner-Riddle, R. Gordon, Ammonia emissions from the field application of liquid dairy manure after anaerobic digestion or mechanical separation in Ontario, Canada. *Agr Forest Meteorol* 258 (2018) 89–95.
- [6] C. Yirong, W. Zhang, S. Heaven, C.J. Banks, Influence of ammonia in anaerobic digestion of food waste, *J. Environ. Chem. Eng.* 5 (5) (2017) 5131–5142.
- [7] J.H. Martin, An evaluation of a mesophilic, modified plug-flow anaerobic digester for dairy cattle manure, Final Report for EPA Contract GS10F-0036K, U.S. Environmental Protection Agency, Washington, DC, 2005.
- [8] L. Zhang, E.G. Xu, Y. Li, H. Liu, D.E. Vidal-Dorsch, J.P. Giesy, Ecological risks posed by ammonia nitrogen (AN) and un-ionized ammonia ( $NH_3$ ) in seven major river systems of China, *Chemosphere* 202 (2018) 136–144.
- [9] A.M. Backes, A. Aulinger, J. Bieser, V. Matthias, M. Quanté, Ammonia emissions in Europe, part II: how ammonia emission abatement strategies affect secondary aerosols, *Atmos. Environ.* 126 (2016) 153–161.
- [10] D.J. Randall, T.K.N. Tsui, Ammonia toxicity in fish, *Mar. Pollut. Bull.* 45 (1–12) (2002) 17–23.
- [11] L.J.M. Van der Eerden, P.H.B. de Visser, C.J. Van Dijk, Risk of damage to crops in the direct neighbourhood of ammonia sources, *Environ Pollut* 102 (S1) (1998) 49–53.
- [12] D. Georgiou, V. Liliopoulos, A. Aivasidis, Investigation of an integrated treatment technique for anaerobically digested animal manure: lime reaction and settling, ammonia stripping and neutralization by biogas scrubbing, *Bioresour Technol Rep* 5 (2019) 127–133.
- [13] G. Provolto, F. Perazzolo, G. Mattachini, A. Finzi, E. Naldi, E. Riva, Nitrogen removal from digester slurries using a simplified ammonia stripping technique, *Waste Manage* 69 (2017) 154–161.
- [14] A. Jiang, T. Zhang, Q.B. Zhao, X. Li, S. Chen, C.S. Frear, Evaluation of an integrated ammonia stripping, recovery, and biogas scrubbing system for use with anaerobically digested dairy manure, *Biosyst Eng* 119 (2014) 117–126.
- [15] W. Huang, Z. Zhao, T. Yuan, Z. Lei, W. Cai, H. Li, Z. Zhang, Effective ammonia recovery from swine excreta through dry anaerobic digestion followed by ammonia stripping at high total solids content, *Biomass Bioenerg* 90 (2016) 139–147.
- [16] V.D. Leite, S. Prasad, W.S. Lopes, J.T. de Sousa, A.J.M. Barros, Study on ammonia stripping process of leachate from the packed towers, *J Urban Environ Eng* 7 (2) (2013) 215–222.
- [17] L. Zhang, Y.W. Lee, D. Jahng, Ammonia stripping for enhanced biomethanization of piggy wastewater, *J. Hazard. Mater.* 199–200 (2012) 36–42.
- [18] I.P. Koronaki, L. Prentza, V. Papaefthimiou, Modeling of  $CO_2$  capture via chemical absorption processes – an extensive literature review, *Renew Sust Energ Rev* 50 (2015) 547–566.
- [19] N. Tippayawong, P. Thanompongchart, Biogas quality upgrade by simultaneous removal of  $CO_2$  and  $H_2S$  in a packed column reactor, *Energy* 35 (12) (2010) 4531–4535.
- [20] D. Georgiou, P.D. Petrolekas, S. Hatzixanthidis, A. Aivasidis, Absorption of carbon dioxide by raw and treated dye-bath effluents, *J. Hazard. Mater.* 144 (2007) 369–376.
- [21] A.I. Adnan, M.Y. Ong, S. Nomanbhay, K.W. Chew, P.L. Show, Technologies for biogas upgrading to biomethane: a review, *Bioeng* 6 (4) (2019) 92–114.
- [22] Q. Sun, H. Li, J. Yan, L. Liu, Z. Yu, X. Yu, Selection of appropriate biogas upgrading technology – a review of biogas cleaning, upgrading and utilisation, *Renew Sust Energ Rev* 51 (2015) 521–532.
- [23] C. Gouedard, D. Picq, F. Launay, P.L. Carrette, Amine degradation in  $CO_2$  capture. I. A review, *Int J Greenh Gas Con* 10 (2012) 244.
- [24] T. Nguyen, M. Hilliard, G.T. Rochelle, Amine volatility in  $CO_2$  capture, *Int J Greenh Gas Con* 4 (5) (2010) 707–715.
- [25] A. Ullah, M.W. Saleem, W.S. Kim, Performance and energy cost evaluation of an integrated  $NH_3$ -based  $CO_2$  capture-capacitive deionization process, *Int J Greenh Gas Con* 66 (2017) 85–96.
- [26] J. Gaspar, M. Waseem Arshad, E.A. Blaker, B. Langseth, T. Hansen, K. Thomsen, N. von Solms, P.L. Fösbøl, A low energy aqueous ammonia  $CO_2$  capture process, *Energy Procedia* 63 (2014) 614–623.
- [27] G. Puxty, R. Rowland, M. Attalla, Comparison of the rate of  $CO_2$  absorption into aqueous ammonia and monoethanolamine, *Chem. Eng. Sci.* 65 (2) (2010) 915–922.
- [28] D. Georgiou, A. Aivasidis, J. Hatiras, K. Gimouhopoulos, Treatment of cotton textile wastewater using lime and ferrous sulphate, *Water Res.* 37 (9) (2003) 2248–2250.
- [29] J. Crittenden, R. Trussell, D. Hand, K. Howe, G. Tchobanoglous, *Water Treatment: Principles and Design*, John Wiley & Sons, 2005.
- [30] T.A. Larsen, K.M. Udert, J. Lienert, Transfer into the gas phase: ammonia stripping, *Source Separation and Decentralization for Wastewater Management*, IWA Publishing, London UK, 2013.
- [31] O. Levenspiel, *Chemical Reaction Engineering*, 3rd ed., John Wiley & Sons, Inc., 1999.
- [32] APHA, E.W. Rice, R.B. Baird, A.D. Eaton, L.S. Clesceri (Eds.), *Standard Methods for the Examination of Water and Wastewater*, 22nd edition, AWWA, WEF, 2016.
- [33] C. Wanga, M. Perry, G.T. Rochelle, A.F. Seibert, Packing characterization: mass transfer properties, *Energy Procedia* 23 (2012) 23–32.
- [34] J.A. Rocha, J.L. Bravo, J.R. Fair, Distillation columns containing structured packings: a comprehensive model for their performance. 2. Mass-Transfer model, *Ind. Eng. Chem. Res.* 35 (1996) 1660–1667.
- [35] J.L. Bravo, J.R. Fair, Generalized correlation for mass transfer in packed distillation columns, *Ind Eng Chem Process Des Dev* 21 (1982) 162–170.
- [36] K. Onda, H. Takeuchi, Y. Okumoto, Mass transfer coefficients between gas and liquid phases in packed columns, *J. Chem. Eng. Jpn.* 1 (1968) 56–62.
- [37] OSHA (Occupational Safety and Health Administration), *Hazard Communication Standard* (29 CFR 1910.1200), (2012) [https://www.osha.gov/pls/oshaweb/owadisp.show\\_document?p\\_id=10099&p\\_table=STANDARDS](https://www.osha.gov/pls/oshaweb/owadisp.show_document?p_id=10099&p_table=STANDARDS).