

Organic Wastes to Increase CO₂ Absorption

Manuel Jiménez Aguilar

Andalusian Institute of Agricultural Research and Training, Andalusian Regional Ministry of Agriculture, Fisheries and Environment, Government of Andalusia, Granada, Spain

Email: manuel.jimenez.aguilar@juntadeandalucia.es

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Abstract

The objective of the study was actually the investigation of the effect of various organic wastes on the ability of urine in absorbing CO₂. Urine alone or mixed with olive-oil-mill waste waters (O), poultry litter (P) or meat bone meal (M) was used on the absorption of CO₂ from a gas bottle. The absorption capacity (1.35 - 2.85 gCO₂/gNH₄) was bigger than other solvents such as ammonia and amines. The range of CO₂ absorption was significantly bigger for the organic mixtures P and PM with urine (9.1 - 11.8) g/L than urine alone 6.5 g/L. These organic wastes could be used to increase CO₂ absorption in urine and reduce gas emissions.

Keywords

Olive-Oil Waste Waters, Urine, Poultry Litter, Carbon Dioxide, Diesel Exhaust

1. Introduction

Global warming resulted from emission of greenhouse gases has received widespread attention. Among the greenhouse gases CO₂ contributes more than 60% to global warming because of its huge emission amount. Though various CO₂ capture technologies including physical absorption, chemical absorption, adsorption and membrane exist, they are not matured yet for post-combustion power plants. Among these technologies chemical absorption using aqueous alkanolamine solution is proposed to be the most applicable technology for CO₂ capture. Alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA), and N-methyldiethanolamine (MDEA) are widely used as absorbents for CO₂ capture [1].

However, the MEA process suffers the following disadvantages for CO₂ separation from flue gases: Low carbon dioxide loading capacity (Kg CO₂ absorbed per Kg absorbent); high equipment corrosion rate; amine degradation by SO₂, NO₂, HCL and HF, and Oxygen in flue gas; high energy consumption during high temperature absorbent regeneration.

An ideal absorbent should have a CO₂ loading capacity of at least 1 Kg of CO₂ per Kg of solution and that the

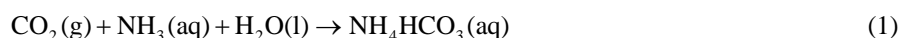
regeneration energy requirement must be much lower than the MEA process. The aqua ammonia process seems to have avoided the shortcomings of the MEA process: Aqueous ammonia has high loading capacity; aqueous ammonia does not pose a corrosion problem; there is no absorbent degradation problem, thus reducing absorbent makeup rate; the energy requirements for absorbent regeneration is predicted to be at least 75% less than in the MEA process [2].

CO₂ removal efficiency and absorption capacity of NH₃ solvent are better than those of MEA. The maximum CO₂ removal efficiency by NH₃ solvent can achieve 99% and the CO₂ absorption capacity can approach 1.2 KgCO₂/Kg NH₃ while for MEA it is only 0.4 KgCO₂/Kg MEA [3].

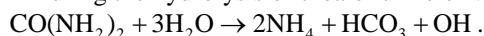
Aqueous ammonia can be used to capture CO₂ from flue gas of coal-fired power plant with quick reaction rate, high removal efficiency, and high loading capacity of CO₂ [4].

However, the absorbents should not be limited to alkanolamines but ionic liquid and other alkaline absorbents as well as the mixtures are also needed to test their potential. The development of suitable absorbents with high CO₂ adsorption capacity is still demanded [5].

In animals ammonia removal is performed through the CO₂ by the urine. On the other hand to increase CO₂ absorption we could think of using any organic residue as a source of ammonia. So, Ammonia in solution from urine has been used to capture CO₂ gas and produce ammonium bicarbonate [6].



During the hydrolysis of urea of urine or waste-water solutions pH is increased and NH₄ produced.



NH₄ is in equilibrium with dissolved and gaseous ammonia. The pKa value for this equilibrium is 9.3 at 25°C.

For other wastes, mineralization is the process by which microbes decompose organic N from manure, organic matter and crop residues to ammonium.

Cumulative net N mineralized in P was fitted to a two-pool, fast and slow first-order models. The fast N pool varied from 11.6% to 56.9% of organic N and could be predicted from uric acid-N-concentration in the litter. Total mineralizable N (fast + slow N pools) range from 46.5% to 86.8% of organic N and could be predicted from uric-acid N and total N concentration. Differences that affect N mineralization rates of P include uric acid concentration (which depends on diet) and moisture content of the litter [7]. Moisture content is particularly important because it supports bacterial activity and thus the production of the enzyme urease, which breaks down uric acid molecules to simpler N forms [8]. Nitrogen mineralization (percent total organic N converted to inorganic N) rates were higher for fresh litter (range of 42% - 64%) than composted litter (range of 1% to 9%) with a relation C/N of 8:1 [9].

M a potential organic fertiliser for agricultural crop contains considerable amounts of nutrients (on average) 8%N, 5%P, 1%K and 10%Ca [10]. The low C/N ratio of M about 4 provides great potential for N mineralization [11]. Soil amendment with M caused a noteworthy increase in both extractable NH₄ and NO₃ (about 50% of added N). The potential of M as effective organic fertilizer was supported by the large increase in available N [12].

If the aqueous ammonia is the agent that can remove CO₂, that may exist in the flue gas [2]. It would possible to think that organic wastes such as P [13] and M [10] like sources of organic N (1%, 8%, respectively) could be added urine and the mineralised ammonium used to increase the capture CO₂. The aim of the present work was to investigate the ability of NH₄ of O, P, and M to increase the CO₂-absorption capacity of urine.

2. Materials and Methods

The urine used in the experiments was my own family urine, pH 5.9 ± 0.3; EC 13.8 ± 3.5; NH₄-N 6 ± 2.3. The O, collected from St. Anthony oil mill of Viznar (Granada, Spain) in January 2013, had a pH of 4.2, EC of 12 dSm⁻¹. The CO₂ came from an industrial gas cylinder supplied by the company Air Products Ltd.

Two samples of 200 mL of hydrolysed urine were used as controls. The different treatments for Sample 1 were: (A-urine alone; AP1-urine mixed with 0.25%P in weight; AP2-urine mixed with 0.5%P in weight; AP1O-urine mixed with 0.25%P in weight and 2.5%O in volume; AP2O-urine mixed with 0.5%P in weight and 2.5%O in volume. For the sample 2 were: (B-urine alone; BM-urine mixed with 0.25%M in weight; BMO-urine mixed with 0.25%M in weight and 1%O in volume; BMP-urine mixed with 0.125%M and 0.125%P in weight; BMPO-urine mixed with 0.125%M and 0.125%P in weight and 1%O in volume. When pH increased above 8.5, the BC half samples were kept 45 minutes in a reactor at a pressure of 6 bar CO₂ (Days 15-22). In the end the pH of pressured samples decreased to around 7.5. Similarly, the AC half samples were kept 40 minutes

in the reactor (Days 11, 13 and 19). All the samples were stored in stove to 25°C for 3 months with two replicates for each treatment.

Every week, the pH, CO₂, and NH₄ values as well as the EC of each sample were measured. The pH was monitored using a pH/ion meter, and EC using a conductivity meter (both Crison 2002). The CO₂ was analysed following the procedure reported by Lin and Chan [14]. For this, after determining the initial pH of the sample, a 2 mL urine sample was pipetted into a vial containing 10 mL of 0.1 N HCl and the mixture was placed in a boiling water bath for 10 min to expel the CO₂. Allow the sample to cool to room temperature, add a magnetic stirrer and titrate with 0.1 N NaOH. Note the volume of NaOH added to achieve the initial pH of the sample. A blank containing 2 mL of distilled water was treated in an identical way. The amount of CO₂ in mEq/L was determined by multiplying the difference in the volumes of NaOH, required to titrate the blank and sample, by the normality of NaOH. The NH₄ was analysed following Nelson [15].

The results were subjected to an analysis of variance and comparison of means using the PC computer program Statistic 8.0 (Analytical Software, FL, USA). Also, the figures were plotted with this program.

3. Results and Discussion

The average values of pH, EC, NH₄, CO₂, CO₂-Absorption and Absorption capacity (CO₂/NH₄) of each treatment are shown in **Table 1**.

In Sample 1, the carbonated treatments increased the CO₂ absorption and EC in all samples, indicating that part of CO₂ (6.6 - 13.9 g/L) was absorbed by the samples (**Figure 1**). The increase in conductivity was generated by CO₂ dissolution and ionisation in water was reduced by the decomposition of urea and NH₄ due to volatilization.

The treatments with the highest CO₂ absorption were AP1C and AP1OC (11.8 - 11.7 g/L) (see **Table 1**, **Figure 1**). This indicates that add a slight proportion of P (0.25% in weight) in urine significantly improves CO₂ absorption. A bigger increase of P (0.5% in weight) does not improve CO₂ absorption. O slightly reduced pH but no influence on CO₂ absorption.

Table 1. Main effects of CO₂ absorption on the pH, EC, CO₂, NH₄ and Absorption capacity for each treatment (average values for 7 measurements).

Treatment	pH	EC (dS/m)	NH ₄ (g/L)	CO ₂ (g/L)	CO ₂ -Absorption (g/L)	Absorption Capacity
A	9.0c	44.6b	6.0ab	8.2a	0	1.3a
AC	8.2ab	48.7bc	7.0bc	14.8b	6.6a	2.1b
AP1	9.0c	35.6a	5.1a	8.4a	2.0a	1.6ab
AP1C	7.8a	57.3d	7.6c	20.6c	13.8c	2.7c
AP1OC	7.8a	56.8d	7.6c	20.6c	13.7c	2.7c
AP2	8.8bc	35.7a	5.1a	10.4a	3.7a	2.0b
AP2C	8.0a	54.5cd	7.6c	19.9c	13.0bc	2.6c
AP2OC	7.7a	55.0d	7.6c	20.8c	13.9c	2.8c
B	9.2c	30.7a	5.5ab	4.2a	0a	0.8a
BC	8.4abc	33.2a	5.3a	10.1b	5.9b	2.0c
BM	9.1c	30.9a	5.4ab	7.4ab	3.2ab	1.4b
BMC	8.3ab	39.7b	6.5bc	17.3c	13.1c	2.7d
BMOc	7.9a	41.8b	7.0c	19.1c	14.9c	2.7d
BMP	9.0bc	30.7a	5.4ab	9.5b	5.2b	1.8bc
BMPC	8.2a	40.8b	6.9c	19.1c	14.9c	2.8d
BMPOc	7.9a	39.2b	6.5bc	18.6c	14.4c	2.9d

Different letters (a, b, c, d) within a column indicate significative differences between treatments at level of significance ($P < 0.05$) according to Tukey's test.

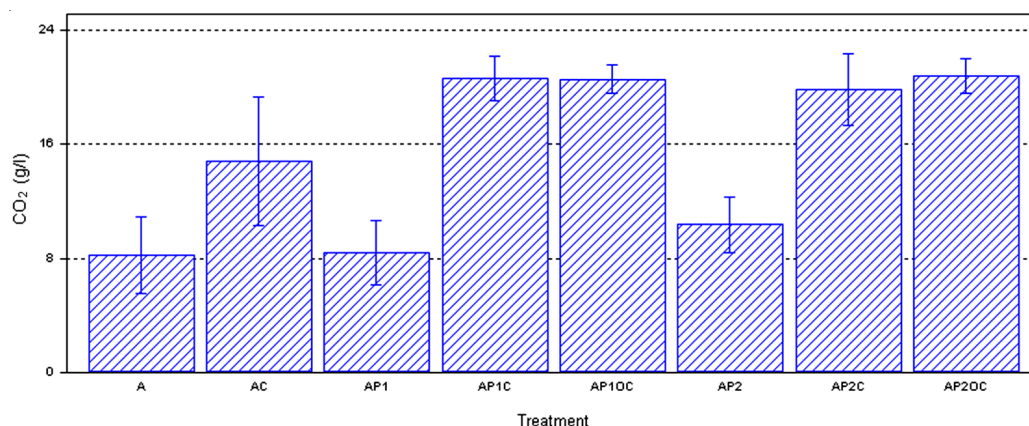


Figure 1. Mean values of CO₂ (Sample 1).

The carbonated treatments increased the mineralised NH₄ in all samples (**Figure 2**). The NH₄ decrease in AP1 and AP2 samples could be explained according to Buondonno *et al.* [16] by the fact that some organic wastes can increase immobilization of inorganic or mineralised N.

In Sample 2, the carbonated treatments increased the CO₂ absorption and EC in all samples, indicating that part of CO₂ (5.9 - 14.9 g/L) was absorbed by the samples.

The treatments with the highest CO₂ absorption were BMOC and BMC (11.7 - 10.0 g/L) (see **Table 1**, **Figure 3**). This indicates that a slight proportion of M (0.25% in weight) or mixtures (0.125%M + 0.125%P in weight) in urine significantly improves CO₂ absorption.

The carbonated treatments increased the mineralised NH₄ in all samples (**Figure 4**). The effect is not as clear as in Sample 1. However, in all cases the absorption of CO₂ causes an increase in free NH₄ with its implications at the agricultural level.

Liu *et al.* [4] study the CO₂ removal efficiencies at room temperature and different concentrations of aqueous ammonia. The best concentration of aqueous ammonia should be selected from 5% - 10%. The CO₂ removal efficiency was 60% in 50 minutes, for a concentration of aqueous ammonia 1%.

In our samples with a concentration of aqueous ammonia smaller than 1%, we should think in an absorption time of about 2 hours to get an efficient removal of 100% CO₂. The absorption time was 120 minutes for sample 1 and 90 minutes for Sample 2. The shorter absorption time (Sample 2 compared to 1), could explain a smaller increase NH₄ and insufficient removal of CO₂.

Theoretically according Equation (1), absorption capacity of ammonia was 2.5 (44gCO₂/17gNH₃). Previous research shows that aqueous ammonia has a higher absorption capacity than that of monoethanolamina (MEA) at same temperature and pressures. Absorption capacity of aqueous ammonia can approach 1.2 KgCO₂/KgNH₃ while for MEA it is only 0.4 KgCO₂/Kg MEA [3].

Our research shows that the absorption capacity of urine was similar to aqueous ammonia (between 0.8 - 1.3 gCO₂/gNH₄). However, the absorption capacity of urine-organic samples mixtures (**Table 1**) is twice (2 - 2.9 gCO₂/gNH₄). These results indicate that the organic samples can reach almost the theoretical value, namely the maximum possible absorption of CO₂ for a given concentration of NH₄ (2.5gCO₂/gNH₄).

The absorbed CO₂ lowered the pH of the urine mixtures due to the formation of carbonic acid. For all the samples, the pH variations could be explained in function of the CO₂ and NH₄ increases. So, the pH, CO₂, and NH₄ showed a statistically significant relationship ($P < 0.0001$) (correlation coefficient 0.624) at the 95% confidence level (see **Figure 5**); NH₄ contributed nearly 2-fold more than CO₂ to the pH variation $\text{pH} = 8.88 + 0.2\text{NH}_4 - 0.12\text{CO}_2$.

The addition of a low percentage of O (acid pH) could reduce urine pH and increase buffering capacity due to fatty acids. To more buffering capacity there is a smaller variation in pH for the addition of CO₂ with a better stabilization of the CO₂ absorbed [6].

NH₄ volatilization increased with the pH, so that all the factors that tended to lower the pH reduced NH₄ losses [17]. Therefore all treatments to reduce the pH proved useful to NH₄ conservation. The addition of a low percentage of O (acid pH) could reduce urine pH and avoid ammonia volatilization [6].

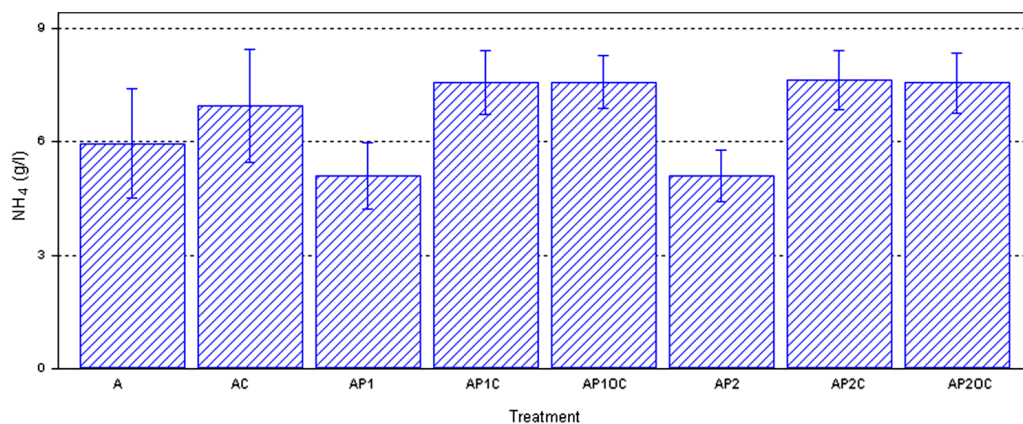


Figure 2. Mean values of NH_4 (Sample 1).

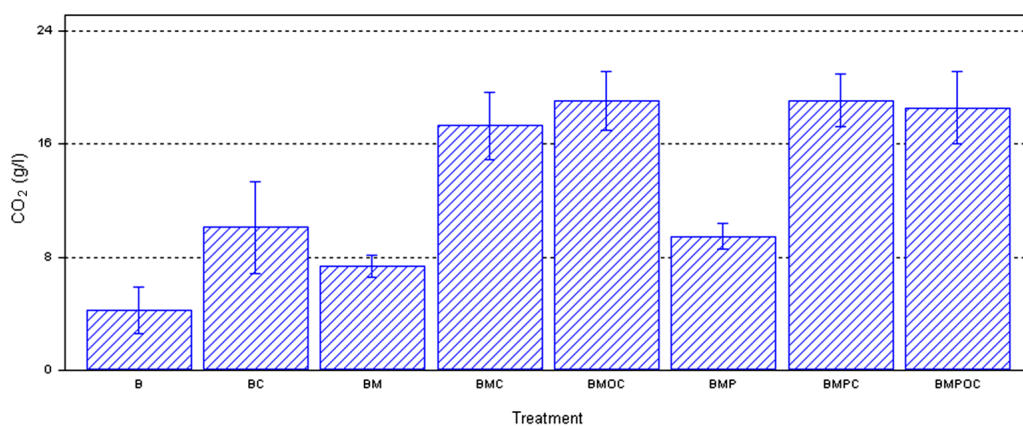


Figure 3. Mean values of CO_2 (Sample 2).

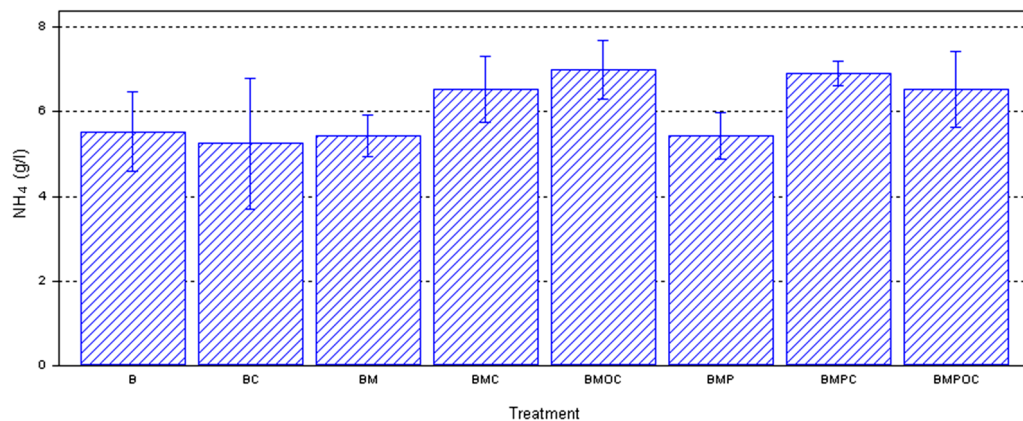


Figure 4. Mean values of NH_4 (Sample 2).

The fact that pH of the carbonated samples reaches a next value to 8.0 could be explain because the mineralization is still producing new NH_4 which is not neutralised by new contributions from CO_2 .

Ammonia availability rate has a fast decreasing after 30 days [7]. In our laboratory, CO_2 and NH_4 contents of all samples treated with CO_2 remained conservative for more than three months.

With the use of organic waste power consumption is minimized because it is not necessary to recover the absorbent again. The CO_2 absorbed by the urine mixtures is fixed to the soil as carbonate or organic carbon through fertilization [18].

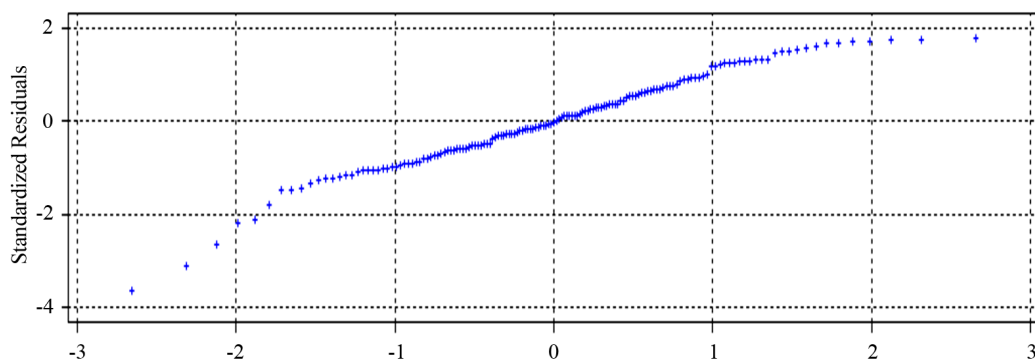


Figure 5. Correlation between pH, CO₂, NH₄.

The advantages of this technology are undeniable: A process for removal of CO₂ at room temperature, without catalyst, with relative low-cost and low-energy requirements. The urine and other wastes produced by a family could be stored and be useful to reduce emissions into towns.

Fertilization with urine and O has previously been demonstrated to be a feasible method for reducing the environmental impact of O and CO₂ [19].

P and M could provide N and other plant nutrients when used as fertilizers. The effects of M as N fertiliser were evaluated by Salomonsson (1994) [20]. In case of spring wheat found no significant differences in grain yields and nitrogen uptake efficiency between M and urea. Diaz, *et al.*, 2008, [13] indicate P like a source of ammonia 11 g/Kg. Thus, urine mixed with the above-mentioned wastes could provide all plant nutrients and be recycled by the fertilizer industry.

However, new wastes, manures, and compost need to be tested with added urine as a means for increasing NH₄ contents and CO₂ adsorption. The proposed strategy requires further research to reduce the risks associated with the waste-water reuse [21].

4. Conclusions

In conclusion, hydrolysed urine mixed with a small percentage (0.25% in weight of P, M, and 1% - 2% in volume of O) could be considered a stable long-term system for greenhouse-gas absorption. The absorption coefficient (1.35 - 2.85 gCO₂/gNH₄) was bigger than other solvents such as ammonia and amines. The range of CO₂ absorption was significantly bigger for the organic mixtures P and PM with urine (9.1 - 11.8) g/L than urine alone 6.5 g/L.

Some organic wastes similar to urine should be tested as CO₂ sinks. In addition, the reduction of CO₂ emissions requires further research to increase the NH₄ contents and CO₂ absorption.

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