



Short communication

Urine as a CO<sub>2</sub> absorbent

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## ABSTRACT

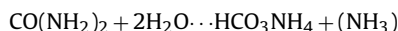
The aim of this work was to investigate the effect of urine on the absorption of greenhouse gases such as CO<sub>2</sub>. Human urine diluted with olive-oil-mill wastewaters (OMW) could be used to capture CO<sub>2</sub> from flue gas of coal-fired power plant and convert CO<sub>2</sub> emissions into valuable fertilizers (mainly, NH<sub>4</sub>HCO<sub>3</sub>) that can enhance CO<sub>2</sub> sequestration into soil and subsoil layers. Thus, the CO<sub>2</sub> emissions could be reduced between 0.1 and 1%. The proposed strategy requires further research to increase CO<sub>2</sub> absorption and assess the risks associated with wastewater reuse and xenobiotics in the agroecological environment.

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## 1. Introduction

Some nutrients consumed in human society today are lost through the sewage. Human urine, a natural resource available in all human societies, is rich in plant nutrients. Urea is the main nitrogen component present in human urine and one of the most important industrial nitrogen fertilizers [1].

The pH of fresh urine ranges from 5.6 to 6.8. The initial pH, and the NH<sub>4</sub><sup>+</sup>-N as well as bicarbonate concentrations, increase with urea hydrolysis due to the decomposition of urea and the formation of ammonia (pK=9.2) and bicarbonate (pK<sub>1</sub>=10.3, pK<sub>2</sub>=6.1). Therefore, the final pH of source-separated urine would be all around 9.0 [2].



Ammonia (NH<sub>3</sub>) released in solution can be used to capture CO<sub>2</sub> gas and produce another one mol of ammonium bicarbonate. The total reaction of aqueous ammonia absorbing CO<sub>2</sub> can be represented as [3]:



Thus, all urea of hydrolyzed urine could be converted to ammonium bicarbonate. In this scenario, atmospheric CO<sub>2</sub> could be absorbed from chimney emissions or concentrations of waste into aqueous solutions.

Ammonium bicarbonate has been used as a nitrogen fertilizer in China for over 30 years. In alkaline soils, the bicarbonate can neutralize alkaline species, such as Ca<sup>2+</sup>, Mg<sup>2+</sup> and reduce the salt content by forming stable species, such as water and calcium–magnesium carbonates. Solid products such as CaCO<sub>3</sub> constitute a stable form of sequestered CO<sub>2</sub>, so that carbonates could react with the alkaline species in groundwater and be deposited as carbonated minerals in the subsoil layers. Once the carbonates from fertilizers enter this type of groundwater, they would not return to the atmosphere for centuries [4].

Olive oil mill wastewaters (OMW) is produced in large amounts in Mediterranean countries. This material must be re-used to reduce the environmental impact and recover some nutrients. To solve the problems associated with OMW management, different elimination methods have been proposed based on evaporation ponds, thermal concentration, and physico-chemical as well as biological treatments, including application to the soil [5,6].

The pH of human-body fluids approaches 7.0 due to the influence of buffer systems, primarily phosphate H<sub>2</sub>PO<sub>4</sub><sup>-</sup>/HPO<sub>4</sub><sup>2-</sup> and bicarbonate HCO<sub>3</sub><sup>-</sup>/H<sub>2</sub>CO<sub>3</sub>. These balances based on the pH can be expressed according to the Henderson–Hasselbalch equation: pH = pK + log[HCO<sub>3</sub><sup>-</sup>]<sub>base</sub>/[H<sub>2</sub>CO<sub>3</sub>]<sub>acid</sub>.

The pK is 6.1 for bicarbonate. Normally, the pH remains close to 7.2, but if the pH falls from 7.4 to 7.1 (log[base/acid] falls from 1.3 to 1) the ratio of bicarbonate:carbon dioxide would drop from 20 to 10. The bicarbonate concentration would be reduced to half or the acid would double.

The pH of OMW drops from 5.5 to 4.2 after 10 months' storage, due to the acid-catalyzed hydrolytic processes which convert fats into fatty acids and acidify the material [7]. Volatile fatty acids such as acetic, propionic, and butyric have a pK close to 4.8.

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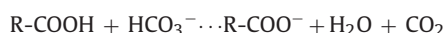
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**Table 1**Main effect of mixtures urine/OMW bubbled with CO<sub>2</sub> on pH, EC, total-CO<sub>2</sub> and free ammonium-N (average values for five months).

Treatment	pH	EC (dS m <sup>-1</sup> )	CO <sub>2</sub> (g L <sup>-1</sup> )	NH <sub>4</sub> <sup>+</sup> (g L <sup>-1</sup> )	dEC (dS m <sup>-1</sup> )	dCO <sub>2</sub> (g L <sup>-1</sup> )	dNH <sub>4</sub> <sup>+</sup> (g L <sup>-1</sup> )
A	8.7a	33.7d	10	5.0	0	0	0
AC	7.66b	43.56a	17.4	6.4	9.86	7.4	1.4
A10%C	7.2c	41.32b	15.0	6.3	7.62	5.0	1.3
A15%C	7.05c	39.51c	13.5	5.9	5.81	3.5	0.9
B	8.64a	22.04b	7.9	3.9	0	0	0
BC	7.57b	26.12a	10.2	4.5	4.08	2.3	0.6
D5%	8.56a	24.87b	8.0	4.6	0	0	0
D5%C	7.36b	31.75a	14.3	6.0	6.88	6.3	1.4

Different letters within a column indicate different levels of significance ( $P < 0.05$ ) according to Tukey's test, A,B: different samples of urine; AC, BC: samples of urine bubbled with CO<sub>2</sub>, A10%C: urine/10%OMW bubbled with CO<sub>2</sub>; A15%C: Urine/15%OMW bubbled with CO<sub>2</sub>, D5%: urine/5%OMW, D5%C: urine/5%OMW bubbled with CO<sub>2</sub>.

The total alkalinity of urine/OMW solutions was owed primarily to bicarbonate alkalinity (i.e. the carbon dioxide/bicarbonate equilibrium) and volatile fatty acid (VFA) alkalinity (i.e. acid/salt equilibrium of acetate, propionate, etc.). As VFA are generated, the bicarbonate alkalinity is consumed and CO<sub>2</sub> is produced, as indicated in equation:



The carbonic acid formed by hydration of CO<sub>2</sub> to react with the alkali salts of buffers generated bicarbonate due to the formation of new molecules of acid, to be removed from the environment when the buffer systems reached their new equilibrium given by isohydric principle.

$$pH = 6.1 + \log[HCO_3^-/CO_2] = 4.8 + \log[A_1/AH_1] = pK_2 + \log[A_2/AH_2]$$

Therefore, the higher the concentration of non-bicarbonate buffers in the environment, more bicarbonate is formed, which corresponds to a smaller variation of pH for the addition of CO<sub>2</sub>, this having more buffering capacity [8].

In the urine/OMW system the buffering capacity increases as the pH decreases compared to physiological values. Therefore, the addition of a small percentage of OMW to urine could help stabilize the CO<sub>2</sub> absorbed, and provide both HCO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> ions a better fixation in the soil. The addition of acidic materials to urine may reduce urea hydrolysis and NH<sub>3</sub> volatilization. Therefore, OMW was useful to reduce pH urine and so NH<sub>3</sub> volatilization. Moreover, the ammonium ion linked with OMW in the presence of carbonates or hydroxides of soil and can be useful for conservation. Besides it can partially block the inorganic-N temporally, reducing the issuance of nitrate in the soil for 2 months [9].

The aim of this work was to evaluate the ability of urine to absorb greenhouse gases such as CO<sub>2</sub>. Also, the effect of a small percentage of OMW in urine on its absorption capacity was investigated.

## 2. Material and methods

The urine used in the experiments was my own family urine, pH  $\pm$  5.9 + 0.26; EC  $\pm$  8.8 + 3.4 dS m<sup>-1</sup>; NH<sub>4</sub>-N  $\pm$  6 + 2.8 g/L, Na  $\pm$  2.73 + 2.53 g/L, K  $\pm$  2.65 + 2.85 g/L, P-PO<sub>4</sub>  $\pm$  174 + 81 mg/L. The OMW, collected from St. Anthony oil mill of Viznar (Granada province, Spain) in January 2010, had a pH of 4.2, EC of 12 dS m<sup>-1</sup>, P-PO<sub>4</sub>  $\pm$  190 mg/L, K  $\pm$  7.9 g/L, and total polyphenols - 3.1 g/L, respectively. The CO<sub>2</sub> came from an industrial gas cylinder supplied by the company Air Products Ltd.

Three samples of 1 L of hydrolyzed urine with the addition of 0, 5, 10 and 15% OMW, respectively, were prepared in brown bottles with two replicates for each treatment. Half of the samples were bubbled with CO<sub>2</sub> from a gas bottle to decrease the pH to around 7.0 and stored in the daylight laboratory for 6 months. Every 10 days, the pH values and EC of each bottle were measured, using a pH/ion meter and a conductivity meter, respectively (both Crison 2002). At the end of storage, the

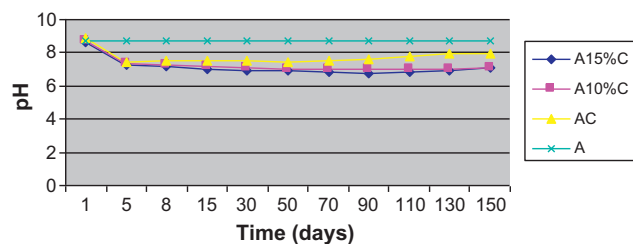


Fig. 1. Evolution of mean values of pH in sample A.

ammonia-N concentration in each sample was determined by distillation using the urea method [10]. For this, 10 ml of potassium phosphate buffer were added to 1 ml of each sample and, after distillation, released ammonia-N was evaluated using diluted sulfuric acid. Bicarbonate was analyzed according to the procedure reported by Lin and Chan [11]. 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 CO<sub>2</sub>. The sample was allowed to cool to room temperature, and the original pH of the urine was titrated with NaOH 0.1 N. A blank, containing 2 ml of distilled water was treated in an identical way. The amount of bicarbonate in mEq/L was determined by the difference in volume of NaOH, required to titrate the sample and blank.

The statistical analysis was performed using the PC computer program Statistic 8.0 (Analytical Software, FL, USA).

## 3. Results and discussion

The average values of pH, EC, ammonium-N and total CO<sub>2</sub> concentrations of each treatment are shown in Table 1. Dissolved CO<sub>2</sub> lowers urine pH due to the formation of carbonic acid, thereby increasing EC, ammonium-N and bicarbonate concentrations. Figs. 1 and 2 show the evolution of mean values of pH and EC in a sample. The other parameters and samples show an evolution similar. Samples urine was bubbled with CO<sub>2</sub> during 5 days to decreasing pH close a 7. After that, all treatments maintained the pH and EC. Everything indicates that ammonium bicarbonate produced could be stored for more than 5 months.

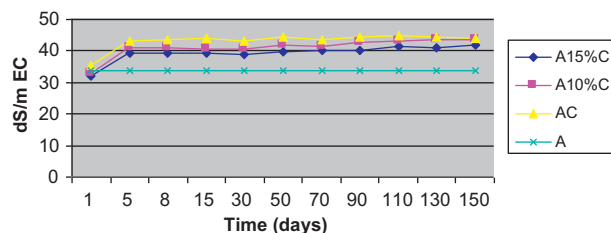


Fig. 2. Evolution of mean values of EC in sample A.

The higher conductivity generated by CO<sub>2</sub> dissolution and ionization in water was used as the analytical response proportional to the content of the gaseous specimen in the sample [12]. This increase in EC together with CO<sub>2</sub>e indicate that part of the CO<sub>2</sub> (2.3–7.4 g) was absorbed by the liter of urine.

The increased EC (dEC) and CO<sub>2</sub> absorbed (dCO<sub>2</sub>) showed a statistically significant relationship (correlation coefficient equals 0.92) at the 95% confidence level:

$$dEC = 2.1 + 0.96dCO_2$$

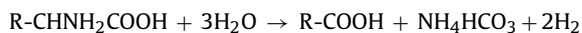
In this work, two different wastewater acids were tested. Because the overall aim of the source-separation system was to use urine as a fertilizer, it would be suitable to use other wastewater acids that could serve as a fertilizer, although not just any acid is useful. Fertilization or irrigation with OMW and CO<sub>2</sub>-water has previously been shown to be a feasible method for reducing the environmental impact of OMW, nitrates, and CO<sub>2</sub> [13]. Also the mixture urine-OMW could be used. Thus, urine, OMW, and CO<sub>2</sub> could be recycled by the fertilizer industry.

Ammonium-N volatilization increased with the pH, so that all the factors that tended to lower the pH reduced ammonium-N losses from volatilization [14]. The urine/OMW dilutions used in our tests, to reduce the pH, decreased the N losses. Moreover, the lower pH could explain the increased ammonium-N due to NH<sub>4</sub><sup>+</sup> formation: NH<sub>3</sub> + H<sup>+</sup> → NH<sub>4</sub><sup>+</sup>

The results of previous studies [15] showed that the addition of hydrolyzed urine to soil resulted in the precipitation of part of the CO<sub>3</sub><sup>2-</sup> as CaCO<sub>3</sub> when the soil pH rose to 8.8, whereas no CaCO<sub>3</sub> formed at pH of 7.1. Between 75% and 95% of the phosphate was recovered from source-separated urine through struvite precipitation when the pH rose from 8.2 to 9.1 [16]. This implies that, since the treatments in the present study maintained the pH below those values, the precipitation of calcite, struvite, and hydroxyapatite in the treatment plants could be reduced.

An increased dissolved carbon dioxide concentration effectively reduces the available alkalinity to offset the metabolism-generated VFA. This could explain that in samples containing urine/OMW the alkalinity was less than with urine alone.

On the other hand, alkalinity increased due to protein breakdown proportional to the quantity of ammonium released, as follows:



That is, 61 g of bicarbonate alkalinity was produced per 16 g of ammonium nitrogen released [17].

Thus, the addition of a small percentage of OMW lowered the pH, increase the buffering capacity and better stabilizing the CO<sub>2</sub> absorbed. In our laboratory this system was stable for more than five months.

The plant nutrients consumed in human society today are lost through the established wastewater-treatment systems in industrialized countries as well as via insufficient or non-existent handling of sewage in the developing world [18]. Separating urine from other sewage at the source reduces the costs of extensive wastewater treatment. Recovering the nutrients from urine and reusing them for agricultural purposes adds resource savings to the benefits [19].

The CO<sub>2</sub> produced per person and day is about 1–10 kg. Thus, if each person's urine were saved (1 L per person per day) with a NH<sub>4</sub>-N average concentration (3–9 g/L) and used to absorb CO<sub>2</sub>, the CO<sub>2</sub> pollution could be reduced between 0.1 and 1%. The increase of pressure on top the gas could increase the absorption. In the house or factory, the own chimneys full up of urine could be used to increase the hydrostatic pressure on CO<sub>2</sub> gas and have a higher absorption capacity.

#### 4. Conclusions

In conclusion, hydrolyzed urine mixed with a small percentage (5–10%) of OMW could be considered a long-term stable system for absorbing CO<sub>2</sub> and producing ammonium bicarbonate as fertilizer. CO<sub>2</sub> absorption capacity of urine (2–8 g/l) could depend of N-ammonium content, percentage of OMW and different conditions of pressure and temperature. The proposed strategy requires further research to increase CO<sub>2</sub> absorption and study the risks associated with wastewater reuse and xenobiotics in the agroecological environment.

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