Research Article

Wastes to Reduce Emissions from Automotive Diesel Engines

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The objective of the study was actually the investigation of the effect of various treatments on the ability of urine in absorbing greenhouse gases. Urine alone or mixed with olive-oil-mill wastewaters (O), poultry litter (P), or sewage sludge (S) was used on the absorption of CO\textsubscript{2} and NO\textsubscript{x} from diesel exhaust. The absorption coefficient (0.98–0.29 g CO\textsubscript{2} / gNH\textsubscript{4}) was similar to other solvents such as ammonia and amines. The ranges of CO\textsubscript{2} absorption (1.7–5.6) g/l and NO reduction (0.9–3.7) g/l in six hours indicate that on average 20 litres of urine could be needed to capture CO\textsubscript{2} and NO\textsubscript{x} vehicle emissions from each covered kilometre. The best results of CO\textsubscript{2} absorption and NO\textsubscript{x} reduction were for urine mixed with O, P and urine alone. These wastes could be used to capture CO\textsubscript{2} and NO\textsubscript{x} from automotive diesel engines to reduce gas emissions. The proposed strategy requires further research to increase CO\textsubscript{2} absorption and reduce the risks associated with waste-water reuse.

1. Introduction

Diesel exhaust consists of a mixture of CO\textsubscript{2}, CO, and nitrogen oxides (NO, NO\textsubscript{x}). In two agricultural tractors, using a portable exhaust-emission analyser, Markisz et al. [1] indicated emission values of CO\textsubscript{2} of 40–80 g/L, NO\textsubscript{x} of 0.4–1 g/L, and CO of 0.2–0.8 g/L. Carbon dioxide is the major greenhouse gas in the world that needs to be reduced. There are various technologies used to separate CO\textsubscript{2} from flue gas. These include chemical solvent methods, physical absorption methods, cryogenic methods, membranes systems, biological fixation, and the O\textsubscript{2}/CO\textsubscript{2} combustion process. The chemical solvent methods are generally recognized as the most effective technologies at present [2].

Nitrogen oxides (NO\textsubscript{x}) are considered to be a major source of air pollution and contribute greatly to photochemical smog, acid rain, ozone depletion, and the greenhouse effect. NO\textsubscript{x} in diesel exhaust is usually composed of >90% NO.

Reduction of nitric oxide flue gas emissions is practised commercially both by the homogeneous process called thermal NO\textsubscript{x} reduction and by heterogeneous processes under the commonly used term “selective catalytic reduction” (SCR). Thermal reduction is usually operated around 900°C, whereas SCR is typically operated at 350°C [3]. Commercial catalysts are honeycomb monolith structures constituted by vanadia and tungsta, the active components, supported on titania [4].

Selective catalytic reduction using urea as a reducing agent has been investigated for about 10 years and currently is a well-established technique to diminish NO\textsubscript{x} emissions originating from heavy vehicles. According to Koebel et al. [5] the main reactions of NO with ammonia and urea produce N\textsubscript{2}, H\textsubscript{2}O, and CO\textsubscript{2}:

\[
4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \tag{1}
\]
\[
2\text{CO(NH}_2)_2 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 4\text{H}_2\text{O} + 2\text{CO}_2
\]

A new mechanism of reaction has been proposed by Nova et al. [4]

\[
\text{NO} + \text{NO}_2 \rightarrow \text{N}_2\text{O}_3
\]
\[
\text{N}_2\text{O}_3 + \text{H}_2\text{O} + 2\text{NH}_3 \rightarrow 2\text{NH}_4\text{NO}_2 \rightarrow 2\text{N}_2 + 4\text{H}_2\text{O} \tag{2}
\]

NO\textsubscript{x} removal by urea over heterogeneous catalyst as well as in the gas phase (homogeneous reaction) has been known to be
very effective to reduce the concentration of such a pollutant. However, the process requires slightly high temperature to decompose urea into NH₃ and facilitate the surface reaction over the catalyst [6].

There is considerable practical interest in developing a modified thermal reduction process that would operate efficiently at lower temperature.

Several investigators refer to such reduction process as “selective non-catalytic reduction” (SNR). SNR refers to NOₓ reduction by means of ammonia (or other reductants) in the presence of mineral surfaces [3]. So, activated carbon was proved to have high catalytic activity for SCR of NOₓ with NH₃ at low temperature. The reduction of NOₓ in air was attempted with urea supported on the activated carbon at room temperature [6].

The mechanism for NOₓ reduction over mineral surfaces may be similar to a mechanism that has been proposed for V₂O₅/TiO₂-SCR catalysts. These main features are the adsorption of NH₃ as NH₄ on the surface, adsorption, and oxidation of NO to NOₓ on the surface, and formation and desorption of the main reaction products, N₂ and H₂O [3].

The main objective pursued in our current study is to establish a process for removal of COᵢ₂ and NOₓ at room temperature without catalysts with relatively low-cost and low-energy requirements. For that, we proposed the hydrolysed urine.

The hydrolysis of urea is catalysed by the enzyme urease, an enzyme of which many microorganisms present in the waste-water solution possess. During the hydrolysis pH is increased and NH₄ is produced:

\[ \text{CO(NH}_2\text{)}_2 + 3\text{H}_2\text{O} \rightarrow 2\text{NH}_4 + \text{HCO}_3 + \text{OH} \]  

NH₄ is in equilibrium with dissolved ammonia:

\[ \text{NH}_4 + \text{OH} \rightarrow \text{NH}_3 + \text{H}_2\text{O} \]  

The pKa value for this equilibrium is 9.3 at 25°C. At the same time dissolved ammonia is in equilibrium with gaseous ammonia. Thus, the decomposition of urea will lead to an increase of NH₄ and pH, and hence there will be a risk of losses of nitrogen through ammonia evaporation [7].

The ammonia from urine can be used to capture CO₂ gas and produce ammonium bicarbonate [8]:

\[ \text{CO}_2 (g) + \text{NH}_3 (aq) + \text{H}_2\text{O (l)} \rightarrow \text{NH}_4\text{HCO}_3 (aq) \]  

If the aqueous ammonia is the agent that can simultaneously remove CO₂, SO₂, and NOₓ plus HCl and HF that may exist in the flue gas [9], it would possible to think that some organic wastes such as P [10] and S [11] like sources of ammonia (11 g/Kg, 2 g/Kg, resp.) could be added urine and used to capture CO₂ and reduce NOₓ emissions from automotive diesel engines.

The acidification is a method to inhibit decomposition of urea and avoid ammonia losses [7]. So, addition of a low percentage of O (acid pH) could stabilize the CO₂ absorbed to reduce urine pH and thus ammonia volatilization [12].

Human urine, O, and P are all materials that are produced in large quantities as wastes of other processes and can be obtained at reasonable prices. Separating urine from wastewater at the source reduces the costs of extensive waste water treatment. The sanitation treatment of solid, dry human faeces would be a much easier process, since it would be more aerobic and the amount of human faeces is low compared to the amount of urine [13]. Recovering the nutrients from urine and other wastes and reusing them for agricultural purposes offer the added benefits of resource savings [14].

The aim of the present work was to investigate the ability of NH₄ from O, P, and S to increase the CO₂-absorption capacity of urine in automotive diesel engines. Also, the effect of bubbled wastes on the germination of tomato seed was tested.

2. Materials and Methods

Five samples of hydrolysed urine were used, at pH 9, 8.4, 8.9, 9, 8.4, and electroconductivity (EC) 25, 15, 42, 25, and 15 dSm⁻¹, respectively. The O, collected from St. Anthony oil mill of Viznar (Granada, Spain) in January 2011, had a pH of 4.2, EC of 12 dSm⁻¹, PO₄-0.19 g/L, K-7.9 g/L, and total polyphenols-3.1 g/L.

Five samples (A, B, C, D, and E) of hydrolysed urine were used as controls. The different treatments were BP-urine mixed with 0.5% P in weight; CS-urine mixed with 0.5% S in weight; DO-urine mixed with 1% O in volume; EPO-urine mixed with 2% O in volume and 1% P in weight. All samples were stored in brown bottles with two replicates for each treatment. Half samples (A1, B1, C1, D1, and E1) were bubbled with fumes from the exhaust pipe of an agricultural tractor (model 996E-Pasquali). For that, each sample was introduced in a 2.5 litre plastic bottle. A curved tube of forge iron communicated the exhaust pipe with the bottom of the bottle. To avoid heating, the ignition engine was switched on/off to intervals of 20 minutes. So, the bubbling time for each sample was 6 hours (2 hours each day during 3 days).

In the end the pH of bubbled samples decreased to around 8.0. All the samples were stored in 1-litre bottles open to air in the laboratory for 5 months. According to Hoglund et al. [15], urine stored for at least 6 months may be considered safe to use as a fertilizer for any crop.

Every two weeks, the pH, CO₂, NH₄, PO₄, and K values as well as the EC of each bottle 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 [16]. 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 [17]. The K⁺ was analysed by direct reading in a flame
2.1. Agricultural Test. In this work, the effects of bubbled wastes on the tomato-seed germination were tested. Preciado et al. [19] studied tomato seedlings watered with four urine dilutions with different levels of EC. The results showed a statistical significance in the growth parameters with the nutrient solution at the level of 1 dS m$^{-1}$.

On the other hand, according to Komilis et al. [20], the O phytotoxicity decreased with increased O dilution with water. The higher the dilution the lower the phytotoxicity. To achieve a EC nearby to 1-2 dS m$^{-1}$ our bubbled samples were diluted to a ratio of 1:10 and 1:20 using tap water. Three seeds from tomato (Solanum lycopersicum) variety Tres Cantos were sown in each plastic cups measuring 7 cm × 5 cm. The plants were grown in a mixture of sand (20 g) and olive stone (5 g). On the first day, 20 mL of tap water was uniformly added to each cup. On alternate days, 5 mL of bubbled wastes dilutions 1/10 or 1/20 or tap water (control) was added to each cup. All samples, including the control, were run in duplicate. The cups were kept in the laboratory for three weeks.

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, CO$_2$, NH$_4$$_4$, PO$_4$, and K of each treatment are shown in Table 1.

The treatments with diesel exhaust increased the CO$_2$ absorption in all samples, indicating that part of CO$_2$ (1.67–5.62 g/L) was absorbed by the samples (Figure 1).

![Figure 1: Mean values of CO$_2$.](image)

The treatment with the highest CO$_2$ absorption were DO1 (5.62 g/L) and urine alone (4.06 g/L) (see Table 1, Figure 1).

Theoretically according to (5), absorption capacity of ammonia was 2.5 (44 g CO$_2$/17 g NH$_4$$_4$). Previous research shows that aqueous ammonia have a higher absorption capacity than that of monoethanolamin (MEA) at the same temperature and pressures. Absorption capacity of aqueous ammonia can be higher than 1 g CO$_2$/g NH$_4$$_4$, and MEA is only 0.36 g CO$_2$/g MEA. The CO$_2$ removal efficiency with 1% aqueous ammonia was 50% in 1 hour [2] (in our research may be similar).

Our research shows that the absorption capacity of urine was similar to NH$_4$ and MEA (between 0.98 and 0.29 g CO$_2$/g NH$_4$ in 6 hours for treatment DO1 and CS1, resp.).

The higher CO$_2$ absorption for DO1 samples could be explained by the buffering capacity of O. To more buffering capacity there are a smaller variation in pH for the addition of CO$_2$ with a better stabilization of the CO$_2$ absorbed [3]. Some treatment significantly reduced NH$_4$ contents (see Table 1, Figure 2).

The decrease in NH$_4$ could be explained by assuming, as indicated by Wei et al. [21], that NO$_x$ from flue gas can...
react with NH$_4$ decomposed from ammonium bicarbonate to produce N$_2$.

The treatments with the lowest NH$_4$ reduction were urine alone (−0.42 g/L) and BP1 (−0.47 g/L). The greatest NH$_4$ decrease in CSI (−2.75 g/L) and DOI (−1.72 g/L) samples could be explained according to Buondonno et al. [22] by the fact that some organic wastes can increase immobilization of inorganic or mineralised N. Moreover, the fact that NH$_4$ ion linked with O in the presence of carbonates would reduce NH$_4$ in DOI and EPO1 samples [12].

If we consider that NH$_4$ lost (0.4–1.7 g/L) in our research was due to NO$_x$ elimination then theoretically between 0.7–3 g/L of NO could be eliminated in 6 hours. So, our NO$_x$ removal efficiency may be similar 80% NO removed in 20–40 hours reported by Shirahama et al. [6].

The dissolved exhaust fumes lowered the pH of the urine mixtures from 9.0 to 8.3 due to the formation of carbonic acid. The lowering of the pH could be explained by the absorption of CO$_2$ on the one hand and the reduction of NH$_4$ values on the other hand.

NH$_4$ volatilization increased with the pH, so that all the factors that tended to lower the pH reduced NH$_4$ losses [23]. Therefore all treatments to reduce the pH proved useful to NH$_4$ conservation.

For all the samples, the pH variations could be explained in function of the CO$_2$ and NH$_4$ increases. So, the pH, CO$_2$ and NH$_4$ showed a statistically significant relationship (P < 0.0001) (correlation coefficient 0.697) at the 95% confidence level (see Figure 3); NH$_4$ contributed nearly 2-fold more than CO$_2$ to the pH variation:

$$\text{pH} = 8.41 + 0.15 \text{NH}_4 - 0.08 \text{CO}_2$$ (6)

The increase in conductivity generated by CO$_2$ dissolution and ionisation in water was reduced by the decomposition of urea and NH$_4$ due to reactions with NO$_x$ [5].

In our laboratory, CO$_2$ and NH$_4$ contents of all samples treated with diesel exhaust remained conservative for more than five months. The better treatments (higher CO$_2$ absorption, with lower NH$_4$ reduction) were DO, A, and BP.

Tables for different vehicles (gasoline, diesel) indicate on average emissions values of 140 g CO$_2$ and 2 g NO$_x$ for kilometre. With these values between 15 and 25 litres of urine could be need to capture CO$_2$ and NO$_x$ mean vehicle emissions from each covered kilometre. The urine produced by a family could be stored at home and be useful to reduce own vehicle emissions into towns.

Nevertheless, the advantages of this technology are undeniable: a process for removal of CO$_2$ and NO$_x$ at room temperature without catalysts with relatively low-cost and low-energy requirements.

Source separation of human urine is based on toilets equipped with two bowls, a front one for the collection of urine and a rear one for faecal material. Separating urine from faeces could have environmental advantages such as the reduction of water consumption for human excrement disposal (make savings 10–20 litres per person and day). Before, the faeces collected separately could be mixed at home with urban organic wastes to produce organic compost. So, both urine bubbled with greenhouse gases and faeces could be used as new fertilizers. The atmospheric CO$_2$ could be absorbed in the urine solutions and added to alkaline soils could be deposited as carbonate minerals.

Some limitations: Urine should be stored at home and carried in the vehicle in a pressure container. Before NH$_4$ contents in urine are variable and depend on diet and ambient temperature which limits the CO$_2$ absorption capacity (about 10 g by litre of urine).

The urine and other wastes containing urea or ammonium bicarbonate such as P by itself could be considered sources of ammonia and useful to CO$_2$ and NO absorption.

3.1. Agricultural Test. The results of the study showed that dilution at the 1:20 level did not significantly diminish the germination or growth of tomato plants for three weeks. Because the overall objective of the source-separation system was to use the wastes as a fertilizer, it would be suitable to test these wastes for different crops over a complete crop cycle. Fertilization with urine and O has previously been demonstrated to be a feasible method for reducing the environmental impact of O, nitrates, and CO$_2$ [24].

P and S could provide N and other plant nutrients when used as fertilizers [25, 26]. Whereas part of added NH$_4$ was consumed to eliminate NO$_x$, the added sources of NH$_4$ (P and S) did not significantly increase CO$_2$ adsorption. Therefore, new wastes, manures, and compost need to be tested with added urine as a means for increasing NH$_4$ contents and CO$_2$ adsorption.

Thus, urine mixed with the above-mentioned wastes could provide all plant nutrients and be recycled by the fertilizer industry.
4. Conclusions

In conclusion, hydrolysed urine mixed with a small percentage (1-2%) of O or P could be considered a stable long-term system for greenhouse-gas absorption. An average of 15-25 litres of these urine mixtures could be needed to capture CO$_2$ and NO$_x$ mean vehicle emissions from each covered kilometre. So, the vehicle exhaust contamination could be reduced. These wastes could be used as fertilizers.

Some wastes similar to urine should be tested as CO$_2$ sinks to produce new carbonated fertilizers. In addition, the reduction of NO$_x$ emissions requires further research to increase the NH$_4$ contents and CO$_2$ absorption.

Conflict of Interests

The author declares that there is no conflict of interests regarding the publication of this paper.

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