academicresearchJournals

Vol. 3(8), pp. 238-244, August 2015
DOI: 10.14662/ARJASR2015.054
Copy©right 2015
Author(s) retain the copyright of this article
ISSN: 2360-7874
http://www.academicresearchjournals.org/ARJASR/Index.htm

Academic Research Journal of Agricultural Science and Research

Full Length Research

Agricultural inputs obtained by CO_2 chemical sequestration in piggery wastewaters

Marieta Ghimpusan[1]*, Aurelia Cristina Nechifor[1], Gheorghe Nechifor[1], Ștefan-Ovidiu Dima[1,2], Piero Passeri[3]

[1] University Politehnica from Bucharest, Faculty of Applied Chemistry and Materials' Science, 1-7 Gheorghe POLIZU, 011061 Bucharest, Romania (* maghimpusan@gmail.com). Corresponding author: Marieta Ghimpusan
[2] National Research and Development Institute for Chemistry and Petrochemistry ICECHIM, 202 Splaiul Independentei, 060021 Bucharest, Romania.
[3] G.O.S.T. Srl, 31 Via Romana, 06081 Assisi (Perugia), Italy

Accepted 13 August 2015

Carbon dioxide sequestration in chemicals with applications in agriculture is one of the active research fields at global scale. The aim of this paper was to study the CO_2 sequestration in piggery wastewater. The obtained products are ammonium carbonate, ammonium bicarbonate, and carbamate, compounds with various agricultural and industrial applications. It was investigated the biological treatment of piggery wastewater for organic carbon and nitrogen removal in a combined anaerobic–aerobic sequestration batch reactor (SBR) system. The wastewater treatment plants are a source of greenhouse gases (GHG) emissions such as CO_2 or nitrous oxide (N_2O). SBR system plant has been proposed as a technology to convert CO_2 and wastewaters into valuable products (hydrogen, methane, organic compounds) by intake of generated gas in the system as a source of reducing power. The laboratory investigation was performed to assess the feasibility of CO_2 absorption and the quantities of Nitrogen-containing compounds decreasing. It was found that by applying this technique, the quantities of organic carbon and nitrogen-containing compounds are significantly reduced. Besides the CO_2 capture and, consequently, the decreasing of GHG amount, the obtained products can find large scale application in agriculture for plant growth, in industry, and even in tissue engineering.

Keywords: carbon dioxide, sequestration, nitrogen, piggery, wastewater.

How to cite this article: Ghimpusan M, Nechifor AC, Nechifor G, Dima S-O, Passeri P (2015). Agricultural inputs obtained by CO2 chemical sequestration in piggery wastewaters. Acad. Res. J. Agri. Sci. Res. 3(8): 238-244.

INTRODUCTION

Livestock is the agriculture branch that is introducing the highest amounts of greenhouse gases (GHG) into the atmosphere, amplifying the global warming, but solutions can emerge right from this problem. The GHGs emissions from agriculture represents 20-35% from the global air pollution, 136 types of gases being found in livestock facilities (Dubeňová et al., 2014; Karandušovská et al., 2011). The two most abundant GHG originating from agriculture are carbon dioxide (CO_2) and nitrous oxide (N_2O). Carbon dioxide is the main greenhouse gas produced during human activities and its concentration is also increasing because of human intervention through deforestation; the forests are well known natural sinks for removing CO_2 from the atmosphere (NRC, 2010). Nitrous

oxide is a compound which appears only in specific conditions of combined aerobic and anaerobic processes of nitrification and denitrification, and it is related to the nitrogen cycle that starts with the transformation of fertilizers and pig manure (Dubeňová et al., 2014). Recent developments in fertilizing formulations are trying to reduce the emission of GHG without reducing the plant nutrition performances (Neamţu et al., 2015; Neamţu, Popescu, & Dima, 2015; Vaz-Patto et al., 2015).

The use as fertilizing agents of products resulted from CO_2 capture in wastewaters is actively studied and shows promising results. Recently, Bonet-Ruiz et al. (2015) reported the CO_2 absorption in a residual sludge rich in ammonia, having as result a fertilizing aqueous stream. Besides the conversion of two residual streams (sludge and CO_2) in a useful fertilization stream, the reported method assures the saving of the energy usually consumed with the recovery of solvent by absorption.

CO_2 sequestration identifies intensive studies in different domains, all aiming to reduce the CO_2 high amounts that cause global warming, ocean acidification, and destabilization of many ecosystems. Besides reforestation and afforestation, the best and greener ways of CO_2 capture, at the moment there are studied the geologic sequestration, absorption in solvents (like monoethanolamine, water), sequestration in oil, gas field, saline aquifer, coal seam, microbial sequestration, biogenic carbonation, ureolytic calcification, and other (Last & Schmick, 2015; Tang et al., 2014; Mahanty et al., 2015). A tangible example from industry can be the CO_2 sequestration by carbonation of artificial gypsum (Perez-Moreno, 2015). Red gypsum is a waste from the radioactive materials' industry and it was used in the mentioned study as calcium source for CO_2 sequestration as calcium carbonate, the most stable form of carbon storage.

Air contaminants emitted from stored animal wastewater affect human health and the environment and, moreover, wastewater treatment plants (WWTPs) are a source of GHG emissions such as CO_2 and N_2O. Thus, the aim of this paper was to analyze the feasibility of CO_2 absorption and nitrogen decreasing by using the CO_2 gas after a biological treatment of a piggery wastewater in a combined anaerobic–aerobic sequestration batch reactor (SBR) system.

MATERIAL AND METHODS

In this study piggery wastewater with pH of 8.70 – 8.93 was collected from the discharged effluent provided by the anaerobically digestion of the mixture of rich straw and swine manures from "Agricola Le Piagge S.s. di Luigi e Fausto", Spello – Italy. A biological treatment was applied to 1000 ml of wastewater sample in a combined anaerobic–aerobic SBR lab system for three weeks. Carbon dioxide was supplied using a lab gas pressurized cylinder. The studied wastewater was regenerated every day and was inoculated with lyophilized bacteria Demstep 50P. Monitoring was carried out by regular sampling and analyses of the wastewater inlet and at the exit of the reactor.

To measure ammonium, nitrite, nitrate and chemical oxygen demand (COD) parameters, photochemical commercial test kits were used, like Hach Lange GmbH, Düsseldorf, Germany LCK type and LANGE Xion500 spectrophotometer. Ammonium, nitrite, nitrate, COD, Total Kjeldahl Nitrogen (TKN), were all measured according to APHA "Standard Methods of Water and Wastewater analysis". Dissolved Oxygen (DO) was measured with a portable Hanna Instruments DO-meter. The chemical oxygen demand, representing the amount of oxygen required to chemically oxidize the substances in the wastewater, was measured using UV-Vis spectrophotometer XION 500, Hach Lange with the test kits Dr Lange LCK 014, 114, 314 after 2 h digestion at 148°C. Total Nitrogen, nitrogen ammonia, nitrite, and nitrate were measured using the kit Dr Lange LCK238, LCK303, LCK342, and LCK339 respectively.

Experiments have been performed at lab scale on the installation presented in Figure 1 and the main results are shown in Table 1.

RESULTS AND DISCUSSIONS

It was found that the values of pH, COD and nitrogen are decreasing during the three weeks experiment. The average raw wastewater, effluent characteristics and plant performance during the period of the test are depicted in Figure 2. Applying this method, the undesired nitrites and nitrates are reduced, fact that that recommends this method for the protection of the environment.

Secondly, it can be seen that the average efficiency of COD removal using the CO_2 gas in the system (the last column) is good compared with the case when CO_2 is not used. After the above described treatment, the effluent parameters are decreasing. The measured DO was 2.60 – 2.73 mg/l.

This interesting trend may be attributed to the reaction mechanism between piggery wastewater contained substances and CO_2. Although the CO_2 absorption mechanism cannot be determined, it still may be expected that one of the main reaction mechanism follows the path: $NH_4^+ \rightarrow NH_3 \rightarrow NH_4HCO_3$.

It is presumed that CO_2 is absorbed by some alkaline substances like the small amount of free NH_3 in the wastewater. The exhaust of free NH_3 will enhance the rate of NH_3 releasing from NH_4^+–N contained in the wastewater. Consequently, NH_3 released in solution can be used to capture CO_2 to generate ammonium

Figure 1. Lab set-up for the study of CO_2 chemical sequestration in piggery wastewaters.

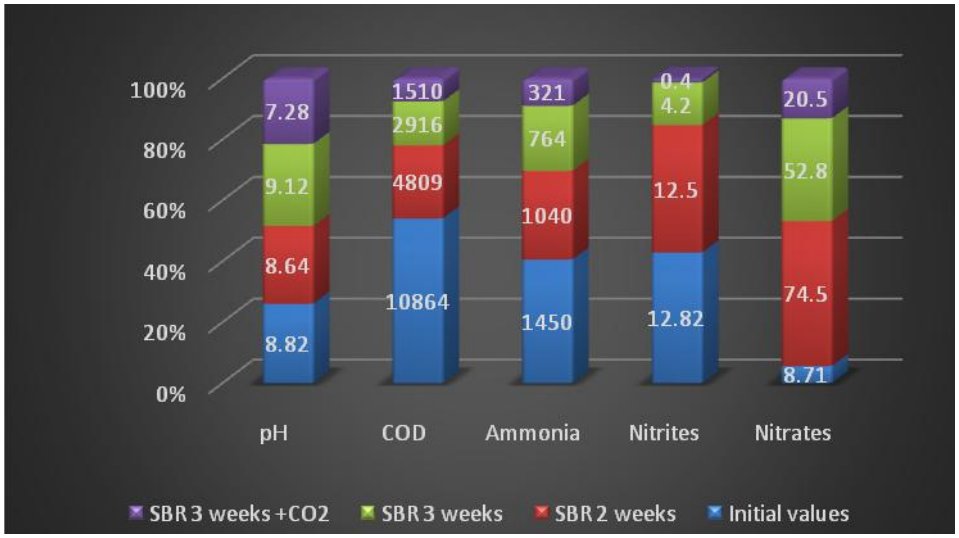

Figure 2. The evolution of parameters' values.

bicarbonate.

For the experimental data was further performed the One Way ANOVA statistical instrument. The Bonferroni's Test was chosen for pair wise multiple mean comparison and Levene's Test for absolute deviations. The results for the statistical analysis are presented in tables 1-3 and in figure 3.

The One Way ANOVA experiment evidenced that at 0.05 significance level, the population means are significantly different. The Bonferroni test takes Sig value

Table 1. Standard deviation and square error of mean for the experimental data.

Descriptive Statistics

	Sample Size	Mean	Standard Deviation	SE of Mean
pH	4	8.465	0.81443	0.40722
COD	4	5024.75	4120.82851	2060.41425
Ammonia	4	893.75	474.58078	237.29039
Nitrites	4	7.48	6.18064	3.09032
Nitrates	4	39.1275	30.0575	15.02875

Table 2. One Way ANOVA

One Way ANOVA

Overall ANOVA

	DF	Sum of Squares	Mean Square	F Value	Prob>F
Model	4	7.56474E7	1.89118E7	5.49527	0.00628
Error	15	5.16222E7	3.44148E6		
Total	19	1.2727E8			

Null Hypothesis: The means of all levels are equal
Alternative Hypothesis: The means of one or more levels are different
At the 0.05 level, the population means are significantly different.

Fit Statistics

R-Square	Coeff Var	Root MSE	Data Mean
0.59439	1.55277	1855.12247	1194.7145

Means Comparisons

Bonferroni Test

	MeanDiff	SEM	t Value	Prob	Alpha	Sig	LCL	UCL
COD pH	5016.285	1311.76968	3.82406	0.0166	0.05	1	705.75996	9326.81004
Ammonia pH	885.285	1311.76968	0.67488	1	0.05	0	-3425.24004	5195.81004
Ammonia COD	-4131	1311.76968	-3.14918	0.06617	0.05	0	-8441.52504	179.52504
Nitrites pH	-0.985	1311.76968	-7.50894E-4	1	0.05	0	-4311.51004	4309.54004
Nitrites COD	-5017.27	1311.76968	-3.82481	0.01657	0.05	1	-9327.79504	-706.74496
Nitrites Ammonia	-886.27	1311.76968	-0.67563	1	0.05	0	-5196.79504	3424.25504
Nitrates pH	30.6625	1311.76968	0.02337	1	0.05	0	-4279.86254	4341.18754
Nitrates COD	-4985.6225	1311.76968	-3.80068	0.01741	0.05	1	-9296.14754	-675.09746
Nitrates Ammonia	-854.6225	1311.76968	-0.6515	1	0.05	0	-5165.14754	3455.90254
Nitrates Nitrites	31.6475	1311.76968	0.02413	1	0.05	0	-4278.87754	4342.17254

Sig equals 1 indicates that the means difference is significant at the 0.05 level.
Sig equals 0 indicates that the means difference is not significant at the 0.05 level.

Table 3. Homogeneity of variance test and the actual power.

Homogeneity of Variance Test

Levene's Test(Absolute Deviations)

	DF	Sum of Squares	Mean Square	F Value	Prob>F
Model	4	2.58747E7	6.46867E6	5.69782	0.0054
Error	15	1.70293E7	1.13529E6		

At the 0.05 level, the population variations are significantly different.

Powers

	Alpha	Sample Size	Power
Actual Power	0.05	20	0.91192

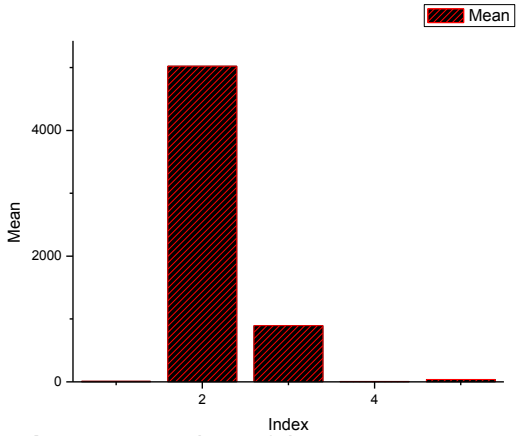

Figure 3. Bar chart of the One Way ANOVA test.

equal to 1 in three cases, all containing COD in their pair: COD-pH, Nitrites-COD, Nitrates-COD, which suggests that these pairs of means are significantly different. The Actual Power value of 0.91 suggests that the probability of rejecting a false statistical null hypothesis is 0.91.

Ramachandran et al. (2006) reported the mechanism for the reaction between CO_2 and primary and tertiary amines and mentioned that a generic chemical reaction has been illustrated by Blauwhoff et al., Versteeg and van Swaaij, Littel et al., and Liao & Li and follows several steps:

Ionization of water

$$H_2O \longrightarrow OH^- + H^+ \quad (1)$$

Dissociation of dissolved carbon dioxide through carbonic acid

$$CO_2 + H_2O \longrightarrow HCO_3^- + H^+ \quad (2)$$

Dissociation of bicarbonate

$$HCO_3^- \longleftrightarrow CO_3^{2-} + H^+ \quad (3)$$

Formation of bicarbonate

$$CO_2 + OH^- \longleftrightarrow HCO_3^- \quad (4)$$

Reaction of CO_2 with nitrogen-containing compounds

$$CO_2 + R_2CH_3N + H_2O \longleftrightarrow R_2CH_3NH^+ + HCO3^- \quad (5)$$

$$R_2CH_3N + H^+ \longleftrightarrow R_2CH_3NH^+ \quad (6)$$

Reaction of CO_2 with primary amine

$$R{-}NH_2 + CO_2 \longleftrightarrow H^+ + R{-}NH{-}COO^- \quad (7)$$

$$R{-}NH_2 + H^+ \longleftrightarrow R{-}NH_3^+ \quad (8)$$

$$R{-}NH{-}COO^- + H2O \longleftrightarrow R{-}NH_2 + HCO_3^- \quad (9)$$

It is considered that this mechanism implies the reaction of primary amines RNH_2 with CO_2 to produce a carbamate RNH_2COO^- by the deprotonation of the base RNH_2COO^-. Any base present in the solution may contribute to the deprotonation reaction. The contribution of each base to the overall reaction rate depends on both its concentration and its strength. Here, R refers to $-CH_2-CH_2-OH$ (Ramachandran et al., 2006).

CO_2 sequestration will continued to be an important research trend, mainly because of the global warming growing concerns. And when the secondary products of CO_2 capture technique have an economical value, that particular technology becomes highly attractive.

CONCLUSIONS

In this paper it was proposed a solution for CO_2 sequestration simultaneously with the production of materials with fertilizing properties and other possible agricultural and industrial applications. A sequestration batch reactor (SBR) system was build in order to investigate the biological treatment of piggery wastewater in a combined anaerobic–aerobic system, followed by CO_2 addition into the reactor in the last step. The experiment lasted three weeks and the obtained products were ammonium carbonate, ammonium bicarbonate, and carbamate. It was found that by applying this technique, the quantities of organic carbon and nitrogen-containing compounds are significantly reduced. The ammonia concentration decreased from 1450 to 321 mg/l, the nitrites concentration decreased from 12.5 to 0.4 mg/l, and the nitrates concentration decreased from 74.5 to 20.5 mg/l. The proposed mechanism under CO_2 influence was: $NH_4^+ \rightarrow NH_3 \rightarrow NH_4HCO_3$. In conclusion, through this technique can be achieved two important objectives: fighting the global warming by decreasing of greenhouse gases through CO_2 secure sequestration, and secondly, valuable products with possible applications in agriculture, food industry, pharmaceutics, plastic industry, and more.

ACKNOWLEDGEMENT

The work has been funded by the Sectorial Operational Programme Human Resources Development 2007-2013 of the Ministry of European Funds through the Financial Agreement POSDRU/159/1.5/S/132395.

REFERENCES

APAT, IRSA – CNR, (2004). Metodi analitici per le acque, ISBN 88-448-0083-7,

Bonet-Ruiz AE, Plesu V, Bonet J, Iancu P, Llorens J (2015). Preliminary technical feasibility analysis of carbon dioxide absorption by ecological residual solvents rich in ammonia to be used in fertigation. Clean Techn Environ Policy. 17:1313–1321

Cortus EL, Gonyou HW, Lemay SP, Barber EM (2005). Measuring and simulating the urination frequency of grower-finisher pigs. Canad J Anim Sci 85:537-539.

Dubeňová M, Šima T, Gálik R, Mihina Š, Vagač G, Boďo Š (2014). Reduction of nitrous oxide and carbon dioxide in the pig barn piggery by different ventilation system intensities. Agron Res 12(1):207–214.

Karandušovská I, Mihina Š, Boďo Š, Reichstädterová T (2011). Produkcia amoniaku a skleníkových plynov v zmodernizovanom objekte ustajnenia dojíc v letom období. Rural buildings 2011: Proceedings of Scientific Works. FE SUA in Nitra. 44–50.

Last GV, Schmick MT (2015). A review of major non-power-related carbon dioxide stream compositions. Environ Earth Sci 74:1189–1198

Mahanty B, Kim S, Kim CG (2015). Dissolved and gaseous inorganic carbon sequestration using a close system cell-free ureolytic calcification process. Environ Earth Sci 73:1473-1477.

Malika M, Islam R, Karim R, Huda A, Jahiruddin M (2015). Organic and inorganic fertilizers influence the nutrient use efficiency and yield of a rice variety BINA dhan7. Acad. Res. J. Agri. Sci. Res. 3:192-200.

Neamţu C, Popescu M, Dima ŞO (2015). Leaching and *in vitro* agrochemical screening for new slow release fertilizers containing N, P, Ca, and Mg. Acad. Res. J. Agri. Sci. Res. 3:45-53.

Neamţu C, Popescu M, Oancea F, Dima ŞO (2015). Synthesis optimization and characterization of microencapsulated NPK slow-release fertilizers. Open Chem. 13(1):813-823.

Ni JQ, Heber AJ, Sutton AL, Kelly DT (2009). Mechanisms of gas releases from swine wastes. Transactions of ASABE 52:2013-2025.

NRC (2010). Advancing the Science of Climate Change. National Research Council. The National Academies Press, Washington, DC, USA.

Olivier JCJ, Janssen-Maenhaut G, Peters JAHW. Trends in global CO_2 emissions; 2012 report. The Hague/Bilthoven: PBL Netherlands Environmental Assessment Agency; 2012. http://dx.doi.org/10.2788/33777

SM Pérez-Moreno, MJ Gázquez, JP Bolívar, (2015). CO_2 sequestration by indirect carbonation of artificial gypsum generated in the manufacture of titanium dioxide pigments. Chem Eng J 262:737–746.

Ramachandran N, Aboudheir A, Idem R, Tontiwachwuthikul P (2006). Kinetics of the Absorption of CO_2 into Mixed Aqueous Loaded Solutions of Monoethanolamine and Methyldiethanolamine. Ind Eng Chem Res 45:2608-2616.

Tang Y, Yang R, Bian X (2014). A Review of CO_2 Sequestration Projects and Application in China. The Scientific World Journal, Article ID 381854.

Vaz-Patto MC, Amarowicz R, Aryee ANA, Boye JI, Chung HJ, Martín-Cabrejas MA, Domoney C (2015). Achievements and challenges in improving the nutritional quality of food legumes. Crit Rev Plant Sci. 34:105-143.