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Use of Cassava Wastewater Treated Anaerobically with Alkaline Agents as Fertilizer for Maize (*Zea mays* L.)

Maria Magdalena Ferreira Ribas[1*], Marney Pascoli Cereda[2] and Roberto Lyra Villas Bôas[3]

[1]Campus do Arenito;Universidade Estadual de Maringá; Rodovia PR 482 km 45; 87820-000; Cidade Gaúcha - PR - Brasil. [2]Centro de Tecnologia de Agronegócios; Universidade Católica Dom Bosco; Instituto São Vicente; 79117-900; Campo Grande - MS - Brasil. [3]Departamento de Recursos Naturais; Universidade Estadual Julio de Mesquita Filho; C.P. 237; 18603-970; Botucatu - SP - Brasil

ABSTRACT

The wastewater of the processing of cassava's flour (manipueira) was submitted to the anaerobic treatment in two phases: acidogenic and methanogenic. In the acidogenic phase, the wastewater was stabilized with NaOH (ASH) and with limestone (ASL). After that, both stabilized effluents were treated by a methanogenic reactor. Then, the effluent of the methanogenic reactor was used as fertilizer on maize in the initial growth stage (30 days), cultivated in pots in a greenhouse. The treatments were T1: control without urea addition (only N from soil); T2: NPK (2.2 g of urea with 45% of N); T3: ASH (84 $mL.kg_{soil}^{-1}$); T4: ASL (102 $mL.kg_{soil}^{-1}$); T5: double dose ASH (168 $mL.kg_{soil}^{-1}$) and T6: double dose ASL (204 $mL.kg_{soil}^{-1}$). Each treatment was composed by 4 plants/pot in five repetitions. It was observed that all the treatments with stabilized wastewater had favorable effect to the soil pH (> than 7.5) and basis saturation (V%) in the soil around to 90%. The performances of nitrogen absorption by the maize plants were 64, 54, 80 and 78% for T3, T4, T5 and T6, respectively.

Key words: Reuse; manipueira, anaerobic digestion, hydroxide sodium; dolomitic limestone

INTRODUCTION

Cassava flour is the main cassava derivative for food use in Brazil and is widely processed in the country. The wastewater is generated in the proportion of 300 L to each ton of cassava root. It is mainly composed of organic matter and nutrients as nitrogen, phosphorus, potassium, calcium, magnesium, sulfur, zinc, manganese, copper, iron and sodium. The organic matter is variable and it can surpass 100 $gCOD.L^{-1}$, with 4 to 6% soluble sugars as sucrose, fructose and glucose (Damasceno et al., 2003). This residue may also contain high cyanide glycoside due to the linamarine decomposition (Cereda and Mattos, 1996; Moraes et al., 2000).

Investigations on the use of the crude wastewater were also proposed considering its use as pesticide (Magalhães et al., 2000), insecticide (Ponte, 2000), heavy metals adsorption (Horsfall Jr and Abia, 2003) and biosurfactants adsorption (Nitschke et al., 2004). The potential use of cassava wastewater as a fertilizer was firstly investigated by Fioretto (2000).

Barana and Cereda (2000) found that the better treatment for this wastewater was in reactors of separated phases (acidogenic and methanogenic). Ribas and Cereda (2003) investigated that in the

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[*] Author for correspondence: m2fribas@yahoo.com.br

acidogenic separated phase, salts of organic acids were formed after neutralization and were commonly sodium hydroxide, calcium hydroxide, sodium carbonate or bicarbonate. Alternatively, the limestone can be a more economic alternative for the pH adjustment, besides producing a fertilizer rich in calcium and magnesium.

The anaerobic effluent may be useful as fertilizer due to its high content of nitrogen and phosphorus, besides, it reduces the needs for commercial fertilizers application (Vazquez-Montiel et al., 1995). According to Jokela et al. (2005), the anaerobic digestion turns soluble organic nitrogen present in the complex matter of the residues, making it available for the plants mainly as NH_4-N. However, it is known that in some particular cases, for instance, crops irrigated with distilleries wastewater do not have the same performance compared with those that had chemical fertilizer because it has inadequate balance in nutrients to that the crop express its full potential growth capacity (Ramana et al., 2002a, 2002b). In this case, it is necessary to complement with chemical fertilizers to guarantee a good yield.

The advantages of the anaerobic effluent irrigation over the crude wastewater use to the soil are to reduce the impacts caused by the chemical fertilizer compounds to promote best soil conditioning. When discarded in the soil, the organic matter of the crude residue competes for the oxygen with the microorganisms and with the plants. Besides, the anaerobic treatment reduces this organic load and produces methane.

Ribas and Cereda (2003) observed that the anaerobic treatment of cassava wastewater was more stable and efficient by use of NaOH and limestone as neutralizing agents in the acidogenic phase. These produced a stabilized effluent with pH 7.0, production of salts of organic acids and conservation of the minerals of the crude wastewater.

Maize (*Zea mays* L.) is chosen as indicative plant for the effluent application effects, because of its high demand in nutrients and it shows the tested fertilizer effects. Ramana et al. (2002b) studied the effects of different distillery effluents on maize plants comparing with the recommended NPK (nitrogen, phosphorus and potassium) + FYM (farm yard manure) and control (no fertilizer or effluent). The study showed that the application of distillery effluents resulted in increases of leaf area, chlorophyll content, nitrate reductase activity, total dry matter and grain yield. Among the effluents, the highest grain yield (after NPK + FYM treatment) was obtained in the treatment with biomethanized wastewater (treated in methanogenic reactor). It was observed that 40 days after sowing, the application of distillery effluents increased the leaf area 40000 $cm^2.m^{-2}$ (NPK+FYM, 50000 $cm^2.m^{-2}$, and control, 20000 $cm^2.m^{-2}$), resulted in higher dry matter production to 350-400 $g.m^{-2}$ by the biomethanized wastewater and of 100 $g.m^{-2}$ by the NPK+FYM in maize.

This work evaluated the impact of the anaerobic wastewater application from a treatment system in two-phases with sodium hydroxide (NaOH) and limestone as stabilization agents on the maize cultivated in a greenhouse in the initial growth stage and on the soil.

MATERIALS AND METHODS

Maize (*Zea mays* L.) seeds: ten seeds (hybrid DKB 250) were sowed in pots filled with 5 kg of clay soil. The rough-hewing was made after the total emergence of the plants, leaving four plants per pot. These plants were monitored for 37 days after the emergence (with just 3 to 5 developed leaves).

Soil analysis: The soil was analyzed according to van Raij et al. (2001). It presented 4.0 $mg.dm^{-3}$ of P, 0.8 $mmol_c.dm^{-3}$ of K, 67.0 $mmol_c.dm^{-3}$ of cation exchange capacity (CEC) and 7% of base saturation level (V%).

Anaerobic wastewater: The irrigation of the plants was done by the application of stabilized anaerobic wastewaters from the anaerobic treatment system of two phases. In the acidogenic phase, sodium hydroxide and dolomitic limestone were used. Then, the effluents of the acidogenic phase passed for the methanogenic phase. Finally, both the effluents were applied in the soil. The electrical conductivity of the wastewater was analyzed by conductivimeter and the nutrients according to the official methods (Standard Methods for the Examinations of Water and Wastewater, 1995).

Soil preparation: Fifty gram of dolomitic limestone with a total neutralization potential of 90% was applied per kg of soil to elevate the base saturation to 70% (Brazilian Agricultural Research Corporation, 1983). Soon after, the pots were incubated for 25 days. In this period, the soil humidity was maintained approximately 80%. After the incubation period, 0.05 g of potassium (using KCl with 60% of K_2O) and 0.34 g of phosphate (using triple super phosphate with 45% of P_2O_5) were added to each kilogram of soil. Treatments: The treatments were: T1 - control without nitrogen; T2 - urea as a nitrogen source; T3 - stabilized effluent application on anaerobic system with sodium hydroxide (ASH) that contained 2.38 g L^{-1} of N; T4 - stabilized effluent application on anaerobic system with dolomitic limestone (ASL) that contained 1.96 g L^{-1} of N. These treatments (T3 and T4) received 0.2 g kg_{SOIL}^{-1} of nitrogen that was sufficient for the development of the maize in initial phase. The plant necessity for the total growth was around 3 g of N, and for 37 days, it would need 1 g N. T5 and T6 were the doses double to that of T3 and T4, respectively. Around of 0.4 g kg_{SOIL}^{-1} of nitrogen was applied with the objective to show the effect of effluent on the maize cultivation (Table 1).

Table 1 – Doses and sources of nitrogen in each treatment.

Treat. #	N source	N amount	N amount applied ($g.kg^{-1}$)	N fertilizer amount
T1	-	-	-	-
T2	Urea	45 %	0.2	2.2 g of urea
T3	ASH	2.38 $g.L^{-1}$	0.2	84 $mL.kg^{-1}$
T4	ASL	1.96 $g.L^{-1}$	0.2	102 $mL.kg^{-1}$
T5	ASH	2.38 $g.L^{-1}$	0.4	168 $mL.kg^{-1}$
T6	ASL	1.96 $g.L^{-1}$	0.4	204 $mL.kg^{-1}$

Evaluation

The soil was evaluated when the plants were 37 days old. The plants were cut at the bottom and their length, stem diameter, fresh matter and dry matter (at 65 ºC) were analyzed. N, P, K, Ca, Mg, S nutrients were also determined (Malavolta et al., 1997). The nitrogen absorption performance was defined as the plants capacity in absorbing N in relation to the absorption in the NPK fertilizer (T2). The nitrogen absorption performance was calculated as following:

$$\varepsilon_N = 100\frac{(N_T - N_{T1})}{N_{T2} - N_{T_1}}$$

where,

NT: accumulated N amount in the plants for different treatments with N (except the T2 with NPK);

NT1: accumulated N amount in the plants for control T1, without N;

NT2: accumulated N amount in the plants for T2 with NPK, whose source of N was urea.

Statistical analysis: Each treatment was composed of five repetitions (five pots), each one with four plants. Data from the above experiments were analyzed by the one-way analysis of variance (ANOVA). The means were separated statistically using the pair wise multiple comparison procedure (Tukey test). Statistical significance was defined as $P \leq 0.05$.

RESULTS AND DISCUSSION

Table 2 showed that the low values of phosphorus in ASL (as P2O5, 0.04 g L-1), were probably due to the phosphorus precipitation by the generation of a calcium phosphate (Morse et al., 1998). However P was not a limiting factor for the maize development as the evaluated period did not coincide with the larger absorption phase during the grains formation and development.

The electric conductivity (EC) was 20 mS cm-1 for the ASH and 17 mS cm-1 for the ASL. These values were considered high compared with nutritious solutions of the fertilizers and vinasse wastewater (cane alcohol distillery wastewater used as fertilizer) having an EC of approximately 1 and 10 mS cm-1, respectively (Ribas et al., 2005).

Effects of the effluents application on the soil

In general, a favorable effect was observed in the soils of T6 that had cation exchange capacity (CEC) of 102 mmolc dm-3 and exchange bases availability (AB) of 96 mmolc dm-3 (Table 3).

Table 2 - Effluent composition anaerobic treated.

Parameter	**ASH**	**ASL**
pH	8.05	7.78
Total solids (%)	4.4	3.7
Total organic carbon (g L^{-1})	17.1	14.6
Carbon (%)	1.4	1.4
Total cyanide (mg L^{-1})	24.5	6.4
N (g L^{-1})	2.38	1.96
K_2O (g L^{-1})	2.02	1.42
Ca (g L^{-1})	0.19	2.22
Mg (g L^{-1})	0.42	2.17
S (g L^{-1})	0.04	0.19
P_2O_5 (g L^{-1})	0.20	0.04
Na (g L^{-1})	9.60	1.80
Cu (mg L^{-1})	0.80	0.20
Mn (mg L^{-1})	0.40	10.40
Fe (mg L^{-1})	0.40	5.20
Zn (mg L^{-1})	9.20	9.00
C/N ratio	6/1	7/1

Table 3 - Soil exchange complex (average of 3 replicates) and electric conductivity (average of 5 replicates) and chemical analysis in the final of the experiment.

Treat.	**EC**	**pH**	**OM**	**P_{RESIN}**	**H+Al**	**K**	**Ca**	**Mg**	**AB**	**CEC**	**V**
#	**(μS cm^{-1})**	**($CaCl_2$)**	**(g dm^{-3})**	**(mg dm^{-3})**	**(mmol$_c$ dm^{-3})**						
1	182	5.3	11 a	47 a	20.0b	0.8a	26a	13a	40a	60a	66a
2	979	4.8	11 a	50 ab	24.0b	1.6a	25a	14a	40a	65a	63a
3	1243	8.1	13 b	106 d	8.0a	6.4bc	27a	20ab	53ab	61a	86b
4	844	7.5	12 b	87 cd	8.3a	5.7b	38ab	34bc	78bc	86ab	90b
5	2982	9.1	12 b	93 cd	5.7a	8.5bc	23a	16a	47ab	53a	90b
6	1799	8.3	12 b	71 bc	6.0a	8.8c	45b	42c	96c	102b	94b
CV%	20.7	5.7	11.9	11.2	21.7	21.3	21.6	26.9	22.6	17.3	5.9

Column means followed by a same letter(s) are not significantly different according to the Tukey test (*P* ≤0.05).

The application of the effluents, both stabilized with NaOH and limestone, increased the pH value of the soil, up to 7.0 for T3, T4, T5 and T6 (Table 3). Longo et al. (1999) also observed that the pH value was slightly higher than 7.0 when a mix of treated anaerobic vinasse and crude vinasse was applied in cultivated soil with sugar cane.

When effluent stabilized with NaOH was used as fertilizer (T3 - ASH in the normal dose), the soil phosphorus (PRESIN) assumed larger amounts compared to the other treatments in spite of this, there was no significant statistical differences with the treatments T4 and T5 (Table 3).

For the exchange bases (Table 3), positive effects of the effluent application (T3, T4, T5 and T6) in potassium, mainly in the treatments T5 and T6, that received the double dose of the respective effluents, were noticed. Freitas et al. (2004) also observed that the P, K, Na, Ca, Mg, Cu and Zn levels increased in the soil with the swine wastewater application, but there was risk of salinity rise in the soil and underground waters. This could be related to the sodium adsorption ratio increase (SAR) that would be more susceptible on irrigated soil with ASH.

Ca and Mg values were also larger in the soils of T6 followed for T4. Probably, this was due to limestone composition that dispersed Ca and Mg ions during the stabilization in an anaerobic acidogenic phase.

The H+Al effect was reduced in the treatments T3, T4, T5 and T with a base saturation level (V%) superior to 80%. Longo et al. (1999) reported that the soils that received a compost vinasse presented the neutralized exchange aluminum, reflecting in the eutrophic characteristic with a base saturation level higher to 50%.

The higher modification in cation exchange capacity values in the soils was found for treatment T6, with ASL in the double dose. T4 did not differ significantly with T6. Cation exchange capacity values and the organic matter of the ASL and ASH treatments indicated that these compounds strongly contributed to the increase in organic composition of the soils.

Fioretto (2000) recommended that the fertilizer practice must be accomplished carefully and in appropriate soils due to the ionic balance. The predominance of the K ion among the constituent minerals of the manipueira has direct implication in the imbalance of the basic cations in the soil because there is an increase of saturation of this element and predisposition to the leaching of Ca and Mg causing unavailability for the plants. An investigation about the residual effects of the manipueira application in a soil (type Dystrophic, clay texture) showed that the excess of K caused unavailability of Mg for the plants in the dose of 160 m3/ha after 90 days of the application (Fioretto, 2000).

Effects of the effluents application on maize

The maize plant's length of the T4 (ASL in normal dose) averaged with 19.2 cm, was lower than other treatments that varied from 26.0 to 28.5 cm. The same treatment presented reduced fresh matter, with a mean value of 2.1 g/plant, but T4 was not different from T1 (control). The average dry matter was 1.2 g/plant that did not differ from the other treatments plants (Fig. 1), except of T2 (urea as nitrogen source). The difference among the stem diameters was not significant (Table 4).

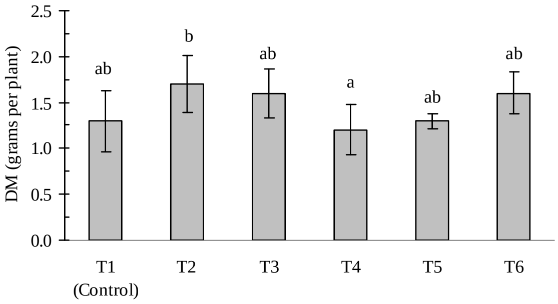

Figure 1 - Maize plants dry matter (DM) after 37 days. Bars having the same letter(s) are not significantly different according to the Tukey test (*P* ≤0.05).

Table 4 - Maize plants length, medium stem diameters, fresh matter with the experimental coefficient of variation (CV).

Treat. #	Length (cm)	Stem diameter (mm)	Fresh matter (g/plant)
1	27.4 b	3.9 a	2.7 ab
2	28.5 b	4.2 a	3.1 b
3	27.1 b	4.8 a	3.5 b
4	19.2 a	4.3 a	2.1 a
5	26.0 b	4.3 a	3.0 b
6	27.6 b	4.3 a	3.4 b
CV%	7.9	16.2	14.9

Column means followed by a same letter(s) are not significantly different according to the Tukey test (*P* ≤0.05).

These results agreed with those obtained by Cezar (2001) that evaluated the effects of different phosphorus sources in two different maize cultivations in the initial phase by dry matter content. The phosphorus fertilization was carried out in a first cultivation, and the second cultivation was carried out to evaluate the residual effect of phosphorus from different sources. It was observed that in the first cultivation, the average value of dry matter was 1.8 g/plant with application of digested swine waste provided with or without phosphorus source. In the second cultivation, this increased to 4.1 g/plant, indicating that successive cultivations were important for the evaluation of the real effects of fertilizers under the plants development.

Table 5 presents foliar chemical analysis after 37 days of growth for the maize aerial part. The nitrogen values on the T2 plants (urea as nitrogen source) were the highest, followed by treatments

T5 and T6 (ASH and ASL in double dose, respectively) that did not differ by Tukey test. The plants without nitrogen (T1) had smaller absorption rates of this element, followed by plants irrigated with ASL (T4) and ASH (T3). Therefore, with the exception of the plants treated with urea the ones that presented better nitrogen absorption were those irrigated with both effluents in double dose (T5 and T6).

Table 5 - The maize plants vegetal chemical analysis after 37 days of emergence. Values represent the three replicate averages.

Treat.	**N**	**P**	**K**	**Ca**	**Mg**	**S**
#			**(g kg^{-1})**			
1	17.3 a	2.4 bc	43.3 bc	6.7 d	4.2 c	2.1 a
2	37.7 d	1.7 a	29.7 a	8.3 e	4.9 d	3.3 b
3	30.3 bc	2.7 c	37.3 b	3.0 b	3.1 b	3.1 b
4	28.3 b	2.0 ab	28.7 a	1.0 a	2.2 a	3.2 ab
5	33.7 c	2.7 c	45.0 c	4.0 c	4.7 cd	2.6 b
6	33.3 c	2.5 bc	42.3 bc	3.0 b	4.7 cd	3.3 b
CV%	4.7	8.9	7.1	7.7	5.4	9.8

Column means followed by a same letter(s) are not significantly different according to the Tukey test ($P \leq 0.05$)

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T3 and T5 treatments (ASH in normal and in double dose, respectively) presented larger phosphorus rates values in the aerial part with no significant difference between them that showed a favorable effect in the plants absorption for phosphorus. However, significant difference was not also observed among the treatments T1, T3, T5 and T6.

Of the four treatments with effluent application (T3, T4, T5 and T6), the T4 plants (ASL) presented lower rates with regard to the nutritional absorption to K, Ca and Mg.

The nitrogen absorption performances relative to the nitrogen absorbed by the maize plants were 64, 54, 80 and 78% for T3, T4, T5 and T6, respectively. The 100% value was attributed to the source urea (T2) as reference index. It was observed that the effluent with limestone applied in the normal dose (T4) was unfavorable, resulting in a smaller nitrogen absorption value. The effluents application in the double dose (T5 and T6) did not affect the nitrogen absorption.

CONCLUSIONS

The effluents application increased the pH value above 7.5 and the exchange bases availability (47 up to 96 mmol$_c$ dm^{-3}) on the soils in comparison to the controls treatments. The application of double doses of both the effluents in these conditions did not affect negatively the maize development in the initial phase of development.

The effluents application promoted larger amount of vegetal nitrogen absorption in the treatments T2 with 37.7 g kg^{-1} (urea), followed by T5 with 33.7 g kg^{-1} (ASH double dose) and T6 33.3 g kg^{-1} (ASL in double dose). The Ca and Mg in soil of the T4, ASL presented smaller amount absorbed by the plants with relationship to the other treatments evaluated.

The cassava wastewater stabilized with limestone could substitute the sodium hydroxide because of its low cost with the advantage of being more adequate for use as fertilizer because of satisfactory vegetal absorption of P, K, Ca and Mg by it. It could be, thus, concluded that the residue used in this work could have potentiality as a fertilizer.

RESUMO

A água residuária do processamento de farinha de mandioca (manipueira) foi submetida ao tratamento anaeróbio em duas fases: acidogênica e metanogênica. Na fase acidogênica, a água residuária foi estabilizada com NaOH (ASH) e com calcário (ASL). Em seguida, ambos efluentes estabilizados foram tratados por um reator metanogênico. Então, o efluente do reator metanogênico foi usado como fertilizante no milho no estádio inicial de crescimento (30 dias) cultivado em vaso em casa de vegetação. Os tratamentos foram T1: controle sem uréia (somente N do solo); T2: NPK (2,2 g de uréia com 45% de N); T3: ASH (84 mL.kg$_{solo}^{-1}$); T4: ASL

(102 mL.kg$_{solo}^{-1}$); T5: dose dupla de ASH (168 mL.kg$_{solo}^{-1}$) e T6: dose dupla de ASL (204 mL.kg$_{solo}^{-1}$). Cada tratamento foi composto por 4 plantas/vaso com 5 repetições. Foi observado que todos os tratamentos com á água residuária estabilizada tiveram efeitos favoráveis ao pH do solo (> que 7,5) e saturação de bases (V%) no solo ao redor de 90%. A eficiência de absorção de nitrogênio pelas plantas foram 64%, 54%, 80% e 78% para T3, T4, T5 e T6, respectivamente.

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