International Journal of Ecology and Environmental Sciences
www.ecologyjournal.in
Online ISSN: 2664-7133; Print ISSN: 2664-7125; Impact Factor: RJIF 5.28
Received: 30-10-2020; Accepted: 14-11-2020; Published: 01-12-2020
Volume 2; Issue 4; 2020; Page No. 567-572

Changes in chemical properties of sandy loam soil and performance of maize with application of primary treated distillery spentwash

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Abstract
The spentwash, an effluent generated from distillery (DSW), even after primary treatment with biomethanation process contains high amount of soluble salts (9.18 ds m^{-1}), organic load [BOD-16057 and COD-28674 mg kg^{-1}], dissolved (1.21%) and suspended solids (1.43%) that exceeds the tolerance limit prescribed by Central Pollution Control Board. To assess the impact of its application on soil properties and crop growth, a laboratory experiment was conducted using loamy sand soil with various quantities of DSW *viz*., 0, 250, 500, 750, 1000 and 1500 m^3 ha^{-1}. The incubation data after 120 days indicated increased soil organic carbon and available plant nutrients *viz*., N, P, K, Ca, Mg, S, Fe, Zn, Mn and Cu content with increased amounts of DSW application. However, the increased pH and soluble salt content cautious the problem of induction of salinity in soil. Further, germination and dry matter accumulation of maize was severely hampered in soils that received DSW at the rate above 500 m^3 ha^{-1} and complete crop failure was observed with 1500 m^3 ha^{-1} application.

Keywords: Dissolved solids, germination, organic carbon, soluble salts

1. Introduction

Spentwash is generated when molasses is subjected to fermentation process to get rectified sprit or ethanol. Molasses is the mother liquor left out from sugar factory after sugar crystallization, which is the raw material for distillery and it contains about 45-50 per cent sugar comprising of disaccharide (Sucrose) and monosaccharide (Glucose and Fructose). The disaccharide present in molasses is first converted into monosaccharides and then converted into alcohol. This process generates 12-15 L of spentwash per liter of ethanol and 220-230 L of ethanol (95%) per tonne of molasses (Asha and Dutta, 1983). The spentwash so obtained is also known as stillage, slops, vinasse, potale or dunder (Sarayu, *et al*., 2009) [23].

The spentwash is a dark brown organic effluent and one of the most complex and strongest organic industrial effluents, having extremely high COD (76,000- 1,08,000 mg L^{-1}) and BOD (32,800- 43,200 mg L^{-1}). Because of the high concentration of organic load, distillery spentwash is a potential source of renewable energy. The spentwash is anaerobically treated in the digester to produce methane a process known as biomethanation. During this anaerobic degradation, the organic matters are converted into Biogas (55% methane) which brings down the substantial organic load and the evolved bio-gas is used as fuel in the boiler (Annon, 2005).

The 295 distilleries in India produce 2.7 billion liters of alcohol and generating 40 billion liters of wastewater annually. The enormous distillery wastewater has potential to produce 1100 million cubic meters of biogas. This massive quantity of effluent, if disposed unscientifically can cause considerable stress on the water courses leading to widespread damage to aquatic life. On other hand it is also considered as potential fertilizer material, as it contains organic matters and nutrient minerals derived from the sugarcane (Kamble, *et al*., 2016) [11]. Also, irrigation water continues to be the single most important factors dictating the success of crop productivity in arid and semi-arid agro-climatic zones. In the past five decades, the water availability has reduced to half and further reduction is fast approaching. This necessitates using every drop of water that can be recycled back to the crop production.

The outcome of research has mixed view on spentwash impact on crop growth and soil properties. The spentwash, a plant originated material, though can serve as source of nutrient to crop may also damage the soil properties (*viz*., increased soil pH, salinity buildup with primary treated spentwash and decreased pH with raw spentwash) and contaminated groundwater if used unscientifically (Rajkishore and Vignesh, 2012) [20]. However, the extent of damage to soil properties with varied quantity of spentwash application is limited. In this context the present research work was carried out with an aim to simulate the varied quantity of spentwash application effect on soil properties and its impact on performance of maize under laboratory condition.

2. Materials and Methods

To study the effect of application of different quantities of distillery spentwash (DSW) on soil properties and maize crop performance, a laboratory incubation study was conducted. The details of material used and methods followed are as described below.

2.1 Characterization of distillery spentwash

Representative primary treated spentwash samples were collected from M/s Chamundi Distilleries Private Limited, Maliyur near Bannur, Mysore district, and were analyzed for pH, BOD, COD, total solids, suspended solids, total dissolved solids, total nitrogen, phosphorus, potassium, chlorides, sodium, calcium, magnesium, sulfur, micronutrients (Zn, Cu, Fe & Mn) and heavy metals (Cd, Ni, Cr and Pb) using standard procedures as given in Table 1.

2.2 Incubation Study

The incubation study was conducted by using sandy laom soil that belongs to Typic Rhodustalf. Two kilogram soils was filled in plastic container and varied amounts of spentwash as indicated below was applied on weight basis.

T1: DSW @ 0 m^3 ha^{-1} (control)
T2: DSW @ 250 m^3 ha^{-1}
T3: DSW@ 500 m^3 ha^{-1}
T4: DSW @ 750 m^3 ha^{-1}
T5: DSW@ 1000 m^3 ha^{-1}
T6: DSW @ 1500 m^3 ha^{-1}

The soils were incubated for 120 days and their chemical properties *viz*, pH, EC, organic carbon, major, secondary and micronutrients were analyzed by following standard procedures (Table 2). The initial properties of soil indicated that the soil pH was neutral and non-saline containing medium amount of available N and P_2O_5 and high in available K_2O (Table 3). The micronutrients content was above critical limit

2.3 Performance of maize

The maize seeds (NAC-6004) were sown to all pots after 120 days of incubation and the impact of distillery spentwash on germination (10 days after sowing) and dry matter accumulation (30 days after sowing) was studied.

3. Results and Discussion

3.1 Characterization of distillery spentwash

The chemical composition of distillery spentwash that was subjected to primary treatment through biomethanation process was neutral in reaction, contained high soluble salts (9.18 dS m^{-1}) and organic load [BOD –16057 and COD-28674 mg kg^1] which exceed the tolerance limit for industrial effluent prescribed by Pollution Control Board (EC < 1 dS m^{-1}, BOD- 100 mg kg^{-1} and COD- 250 mg kg^{-1}) (Table 4). It also had high dissolved (1.21%) and suspended solids (1.43%), which are well above the prescribed level (2,100 mg L^{-1} for dissolved solids and 200 mg L^{-1} for suspended solids), indicating its potential threat to pollute the water bodies and lands if discharged unscientifically. These become limiting factors in utilizing it as nutrient source to crops as unscientific usage may create problem in nutrient uptake and root respiration, besides creating salinity problem in soil (Sahai, *et al*., 1982, Zalwadia, *et al*., 1997, Sukanya and Meli, 2004) [22, 29, 27].

The proximate analysis of spentwash indicated that it contained all the nutrient elements that were absorbed by the sugarcane crop used as raw material for production of array of products in sugar industries *viz*., sugar, mollase, rectified spirit. It has very high amount of potassium (1.15%) and appreciable quantities of nitrogen (0.11%), calcium (1700 mg kg^{-1}), magnesium (1334 mg kg^{-1}) and sulfur (387.8 mg kg^{-1}). But it was poor in phosphorus (0.02 per cent) and micronutrients. Spentwash contains almost all the essential nutrients required by plants. Thus, with careful management practices can be used as liquid organic fertilizer (Madrod *et al.,* 1986, Mallika, 2001) [14, 15]. Besides, the heavy metal content in spentwash is negligible, thus it is safe for using as nutrient source to food crops.

3.2 Effect of spentwash application on electro-chemical properties of soil

Increased quantity of DSW application increased the pH, EC and organic carbon content of soil (Fig.1). After 120 days of incubation, pH of soil has increased from initial 7.24 to as high as 8.73 with application of 1500 m^3 ha^{-1} DSW. The increase in pH might be due to addition of substantial amount of calcium, magnesium and bicarbonates following DSW application. Similar findings of increased pH with application of DSW were reported by Scandaliaris, *et al.* (1987) [24] and Hati, *et al.* (2005 [9]). The spentwash application resulted in accumulation of soluble salts above the critical limit (1 dS m^{-1}) indicating the problem of salinity in soils. Spentwash contains high EC of 9.18 dS m^{-1} and thus increased levels of DSW application to soils results in high build up salt (Patil, *et al.*, 2000 [18]). Soil organic carbon (OC) build up was not significant with lower rates (500 m^3 ha^{-1}) of DSW application as compared to control. This might be attributed to the presence of easily decomposable carbonaceous material in spentwash. Though, spentwash contain high organic load, upon application to soil it will undergo rapid decomposition to release CO_2 (Biswas, *et al.,* 2005a) [5]. Also, spentwash contain very less amounts of humic and fulvic acid (Arafat Sayed and Yassen Abd Elazin, 2002 and Ramadurai and Gerard, 1994) [21], which determines the OC build up in soil due to its resistance to decomposition. However, large quantity of DSW application resulted in substantial OC buildup owing to higher salinity in soil that reduces decomposition process. Biswas *et al.* (2005b) [6] reported higher per cent of C loss as CO_2 with low level of DSW application compared to higher levels and it would take 12 weeks to decompose 50 per cent of added C following DSW application.

3.3 Effect of spentwash application on nutrient content in soil

Application of DSW upto 1000 m^3 ha^{-1} increased the available N content in soil and further increasing the quantity to 1500 m^3 ha^{-1}resulted in decreased available N (Fig.2). Reduced mineralization (Biswas, *et al.*, 2005a) [5] associated with high salt build up and N immobilization due to wide difference in C and N content (Calderon, *et al.*, 2004) [7] might have decreased N content with higher dose of DSW application. Application of DSW upto 1000 m^3 ha^{-1} of DSW increase in P content and further increase in the quantity of DSW brought marginal decrease in P. This might be due to reduced mineralization and probability of P sorption and precipitation with $CaCO_3$ content (Patil and Shinde, 1995) [17]. Increased level of DSW application brought almost linear increase in the available K content in soils. This may be attributed to the presence of high K (1.15%) in spentwash in ionic form that upon application to soil will result in enormous buildup of K on exchangeable sites as well as soluble salts in soil solution and voids. The results are in line with Somashekar, *et al.* (1984) [25] and Patil, *et al.* (2000) [18] who observed increased availability of K with increasing levels of DSW application.

The increased exchangeable Ca^{2+} and Mg^{2+} was observed (Fig. 3) with increased amounts of DSW application might be due to the presence of substantial amounts (1700 mg kg^{-1} and 1344 mg kg^{-1} respectively) in spentwash. Similarly available S content of soils

increased significantly with application of DSW at different quantities due to presence of good quantity of S in DSW (Zalwadia, *et al.*, 1997 [29]).
Significant accumulation of DTPA-Fe, Mn and Cu was observed with increasing levels of DSW application (Fig. 4) owing to its content in DSW (Zalwadia *et al.*, 1997 [29]; Sukanya and Meli 2004) [27]. However, DTPA-Zn content of soils did not differ significantly. A marginal increase in DTPA-Zn was observed with increased DSW application in all soils compared to their initial values.

3.4 Effect of spentwash application on germination and dry matter yield of maize

The Germination of maize seeds reduced significantly with increased quantities of DSW application (Table 3) and 1500 m^3 ha^{-1} application recorded zero per cent germination as compared to 100 per cent germination in control (T_1). This high salt content in soil might have resulted in plasmolysis of endosperm in seeds thus recording poor germination. Poor germination with increased levels of DSW application was noticed by Rajaram and Janardhan (1988) [19], Hari, *et al.* (1994) [8] and Lakshmann and Gopal (1996) [12].
Similarly the dry matter yield was drastically reduced with increasing levels of DSW application. Plants could not establish in soil that received 1500 m^3 ha^{-1} DSW and very poor yield was recorded with 1000 m^3 ha^{-1} DSW application. This might be due to high salt content and coarse texture (Loamy sand), which failed to withstand the adverse effect (high organic and salt load) of DSW. Lakshmann and Gopal (1996) [12] noticed decreased vigour index of maize, sorghum, black gram and cotton seedlings with increased rate of spentwash application and highest vigour index was noticed in 20 times diluted DSW treatment.

Table 1: Methods followed for the analysis of primary treated distillery spentwash

Parameters	Methods	References
pH	Potentiometric method	Manivasakam, 1987
EC (dS m^{-1})	Conductometric method	Manivasakam, 1987
Total, dissolved and suspended solids (%)	Gravimetric method	Manivasakam, 1987
COD (mg L^{-1})	Potassium dichromate method	APHA, 1975
BOD (mg L^{-1})	Iodometric method	APHA, 1975
Carbonates (meq L^{-1})	Titration method using phenolphthalein indicator	Manivasakam, 1987
Bicarbonates (meq L^{-1})	Titration method using methyl orange indicator	Manivasakam, 1987
Total phosphorus (%)	Chloromolybdic acid blue colour method	Manivasakam, 1987
Total potassium (%)	Flame photometry	Manivasakam, 1987
Calcium (meq L^{-1})	Versenate titration method	Manivasakam, 1987
Magnesium (meq L^{-1})	Versenate titration method	Manivasakam, 1987
Sulphur (mg L^{-1})	Turbidimetry	Manivasakam, 1987
Sodium (mg L^{-1})	Flame photometry	Manivasakam, 1987
Chlorides (mg L^{-1})	Winkler's method using potassium chromate as indicator	Manivasakam, 1987
Fe, Mn, Zn and Cu (mg kg^{-1})	Atomic absorption spectrophotometry	Manivasakam, 1987
Cd, Pb, Cr and Ni (mg kg^{-1})	Atomic absorption spectrophotometry	Manivasakam, 1987

Table 2: Methods followed for the analysis of soil samples

Parameters	Methods	References
pH	Potentiometric method	Jackson, 1973
EC (dS m^{-1})	Conductometric method	Jackson, 1973
OC (%)	Wet oxidation method	Walkey and Black, 1934
Avail. N (kg ha^{-1})	Alkaline potassium permanganate method	Subbiah and Asija, 1956
Avail. P_2O_5 (kg ha^{-1})	Olsen's extractant method, Colorimetry	Jackson, 1973
Avail. K_2O (kg ha^{-1})	N NH_4OAC extractant method, Flame photometry	Jackson, 1973
Exch. Ca [cmol (p^+) kg^{-1}]	Versenate titration method	Jackson, 1973
Exch. Mg [cmol (p^+) kg^{-1}]	Versenate titration method	Jackson, 1973
Exch. Na [cmol (p^+) kg^{-1}]	N NH_4OAC extractant method, Flame photometry	Jackson, 1973
Avail. S (kg ha^{-1})	$CaCl_2$ extractant method, Turbidimetry	Black, 1965
DTPA extractable Fe, Mn, Zn and Cu (mg kg^{-1})	Atomic absorption spectrophotometry	Lindsay and Norvell, 1978

Table 3: Initial properties of experimental soil

Soil Parameters	Value	Soil Parameters	Value
Taxonomic name	Typic Rhodustalf	N (kg ha^{-1})	335.6
Coarse sand (%)	53.3	P_2O_5 (kg ha^{-1})	44.36
Fine sand (%)	26.2	K_2O (kg ha^{-1})	410.3
Silt (%)	8.2	Ca [cmol (p+) kg^{-1}]	3.26
Clay (%)	12.3	Mg [cmol (p+) kg^{-1}]	1.85
Textural class	Loamy sand	Na [cmol (p+) kg^{-1}]	0.39
Field capacity (%)	15.2	S (kg ha^{-1})	13.06
CEC [cmol (p^+) kg^{-1}]	7.3	Fe (mg kg^{-1})	48.54
pH (1:2.5)	7.24	Mn (mg kg^{-1})	21.75

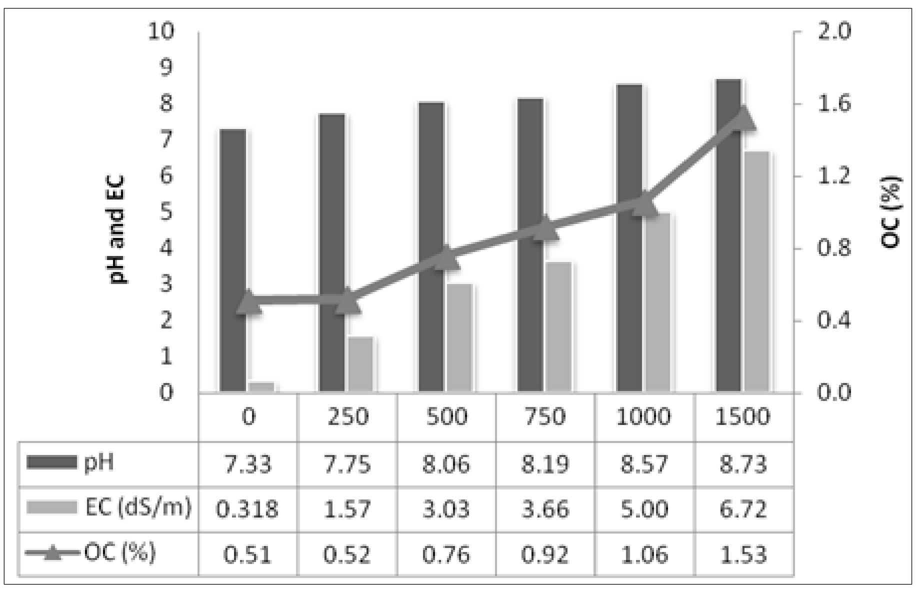
EC (dS m^{-1})	0.226	Cu (mg kg^{-1})	3.10
OC (%)	0.57	Zn (mg kg^{-1})	1.42

Table 4: Chemical characteristics of primary treated distillery spentwash

Parameters	Average Value	Parameters	Average Value
pH	7.22	Total Ca (mg L^{-1})	1700
EC (dS m^{-1})	9.18	Total Mg (mg L^{-1})	1344
TS (%)	2.64	Total S (mg L^{-1})	387.8
TDS (%)	1.21	Total Na (mg L^{-1})	1083
SS (%)	1.43	Total Fe (mg L^{-1})	11.34
COD (mg L^{-1})	28674	Total Mn (mg L^{-1})	1.89
BOD (mg L^{-1})	16057	Total Zn (mg L^{-1})	1.79
HCO_3^- (mg L-1)	167	Total Cu (mg L^{-1})	0.3
Cl^- (mg L^{-1})	5946	Total Cd (mg L^{-1})	0.04
Total N (%)	0.11	Total Cr (mg L^{-1})	0.06
Total P_2O_5 (%)	0.02	Total Ni (mg L^{-1})	0.23
Total K_2O (%)	1.15	Total Pb (mg L^{-1})	0.48

Table 5: Germination and dry matter yield of maize sown in soil after 120 days of distillery Spentwash application

Treatments	Germination (%)	Dry matter yield (g $plant^{-1}$)
T1- DSW @ 0 m^3 ha^{-1}	100 (10.00)	0.414(0.94)
T2-DSW @ 250 m^3 ha^{-1}	66.7 (8.20)	0.503 (0.99)
T3-DSW @ 500 m^3 ha^{-1}	66.7 (8.20)	0.431 (0.96)
T4-DSW @ 750 m^3 ha^{-1}	33.3 (5.81)	0.296 (0.89)
T5-DSW @ 1000 m^3 ha^{-1}	16.7 (4.15)	0.041 (0.74)
T6-DSW @ 1500 m^3 ha^{-1}	0.0 (0.71)	0.000 (0.71)
Mean	36.7 (5.40)	0.254 (0.86)
S.Em ±	0.259	0.018
CD (p=0.05)	0.748	0.051



(Figures in parenthesis indicates transformed value)

Fig 1: Soil pH, EC (dS m^{-1}) and organic carbon (%) as influenced by various quantities of spentwash application after 120 days of incubation.

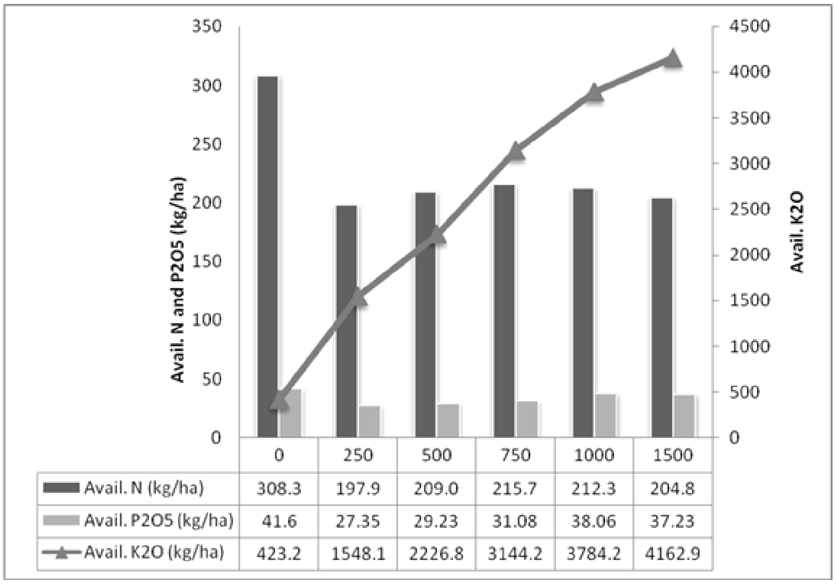


Fig 2: Soil N, P_2O_5 and K_2O content (kg ha^{-1}) as influenced by various quantities of spentwash application after 120 days of incubation

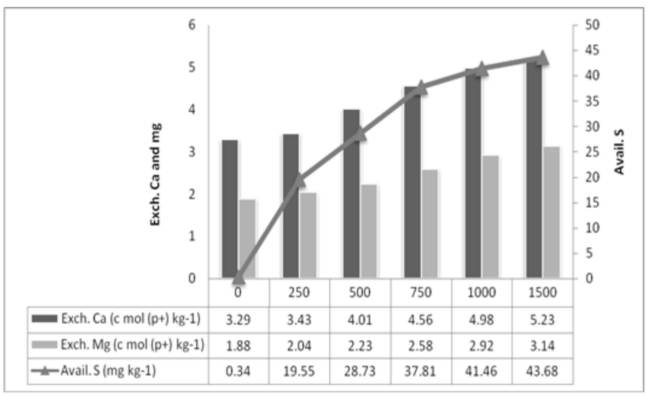


Fig 3: Exchangeable Ca^{2+} & Mg^{2+} [c mol (p^+) kg^{-1}] and available S (mg kg^{-1}) content as influenced by various quantities of spentwash application after 120 days of incubation

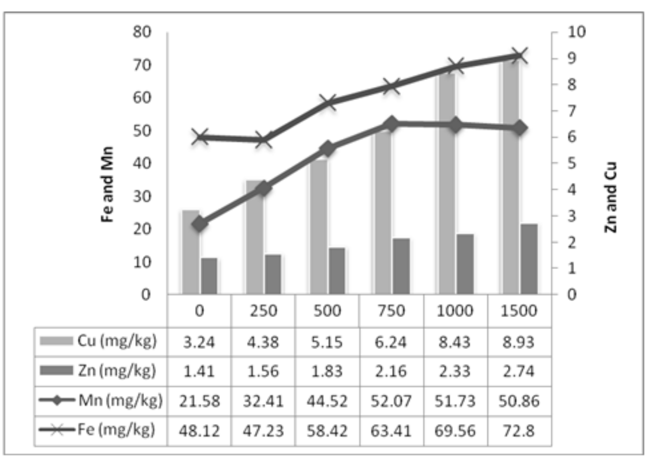


Fig 4: DTPA extracted Fe, Mn, Zn and Cu content (mg kg^{-1}) in soil as influenced by various quantities of spentwash application after 120 days of incubation

Conclusion

The present study indicates that primary treated distillery spentwash is rich source of plant nutrient but contains high salt and organic load. One time application of DSW to sandy loam textured soil though enhanced soil fertility but application rate above 250 m^3 ha^{-1} induced the problem of salinity and adversely affected maize germination and dry matter accumulation.

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