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Influence of distillery spentwash on the physico – chemical properties of calcareous sodic soil (*Calcic natrustalfs*)

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Spentwash is an acidic liquid, rich in organic carbon, Ca, Mg, S and K with considerable amounts of N, P and micronutrients. The composition of spentwash indicated the scope of utilizing it as an amendment for the reclamation of sodic soil and as a cheaper source of plant nutrients. An incubation study was conducted to assess the changes brought in the properties of soil after the application of spentwash at 0, 55, 110 and 225 ml kg^{-1} soil. The samples were analysed for various physico chemical properties such as pH, EC, $CaCO_3$,CEC, ESP, SAR and inorganic carbon contents. Application of spentwash @ 55,110 and 225 ml kg^{-1} soil were found equally effective in reducing the pH of air dried soil to = 8.3 during the incubation period of 60 days. The EC increased progressively and significantly with increasing rates of spentwash application. The ESP decreased from 32.3 to < 14 and SAR from 11.7 to < 8.0 for all the levels of spentwash. The addition of organic matter through spentwash enhanced the organic carbon content of the soil from 0.24 per cent to 0.62 per cent thus increasing the availability of nutrients to the soil.

Key Words: Spentwash, pH, EC, $CaCO_3$, dsp, SAR, Organic carbon

INTRODUCTION

During the recent years, India has emerged as the largest sugar producer of the world. Molasses, one of the byproducts of sugar industry is used for producing alcohol. There are 285 distilleries in India producing 2.7 billion litres of alcohol annually and generating about 40 billion litres of spentwash (Joshi *et al.* 1996). The spentwash which is a waste byproduct of distilleries is a dark brown coloured liquid with unpleasant odour of burnt sugars. It is acidic and highly saline with high BOD, COD, total solids, and other organic compounds like phenols, lignin, oil and greases. Besides, spentwash also contains large amounts of organic carbon, K, Ca, Mg and S and moderate levels of N and P and small quantities of Fe, Mn, Zn and Cu. Since spentwash is an acidic liquid with acid forming character and contains considerable quantities of Ca and Mg, it could be used as a good ameliorant for reclaiming sodic soil besides its usage for the preparation of biocompost using pressmud. At the same time, indiscriminate use and injudicious application of spentwash will affect the soil health and crop growth.With this background in view, a preliminary laboratory incubation study was undertaken to assess the impact of spentwash on the physico chemical properties of calcareous sodic soil besides improving its fertility status.

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MATERIALS AND METHODS

Processed soil samples 500 g each were taken in 400 cm^3 plastic cups and the spentwash at the rate of o, 55, 110, 225 ml kg^{-1} soil equivalent to one time application of 0, 125, 250 and 500 m^3 spentwash ha^{-1}, respectively was added and thoroughly mixed with the soil. Wherever necessary, required quantity of distilled water was added to the soils to attain a final moisture content equivalent to field capacity. The moisture content was corrected at weekly intervals and maintained through out the incubation period. The plastic cups were covered with plastic lids containing small pin-sized holes to permit aeration. Four replicates of each treatment were prepared, randomly placed in tray and kept in the laboratory at 25+2^{0}C for 60 days. Initially and on 15th, 30th, 45th and 60th days of incubation sub samples were removed from each replication and the fresh samples were used for chemical analysis. Moisture factor was computed and applied to express the results on oven-dry basis. The details of the incubation study are presented below:

Treatments :

*Factor A - *Levels of spentwash*

S_0 - No spentwash
S_1 - Spentwash @ 55 ml kg^{-1} soil
S_2 - Spentwash @ 110 ml kg^{-1} soil

S_3 - Spentwash @ 225 ml kg^{-1} soil

*55, 110 and 225 ml of spentwash kg^{-1} soil equivalent to 125, 250 and 500 m^3 of spentwash ha^{-1} respectively, to 125, 250 and 500 m^3 of spentwash ha^{-1}, respectively.

Factor B - Period of sampling (days) :

D_0 - On the day of application
D_1 - 15th day
D_2 - 30th day
D_3 - 45th day
D_4 - 60th day

The present study was carried out in the Department of soil science and Agricultural Chemistry, Agricultural College and Research Institute, Madurai in a completely randomized design.There were totally 80 incubation cups involving four levels of spentwash with four replications and five periods of sampling.The soil samples were analysed for pH and EC (Jackson, 1973). Ten gram of soil sample was treated with an excess standard 0.2 N HCl and back titrated the unreacted acid with standard alkali to determine the presence of free $CaCO_3$ (Piper, 1966). The ESP and SAR of the soil was calculated by using the formulae given by USDA (1954)

$$ESP = \frac{\text{Exch. Na in c mol } (p^+) \, kg^{-1}}{\text{CEC in c mol } (p^+) \, kg^{-1}} \times 100$$

$$SAR_{1:2.5} = Na / [1/2 \, (Ca + Mg)]^{0.5}$$

The cation exchange capacity was determined by replacing the adsorbed sodium with ammonium acetate (Bower and Wilcos, 1965).The organic carbon content of this soil was estimated by chromic acid wet digestion method as prescribed by Walkely and Black (1934).

RESULTS AND DISCUSSION

Characteristics and composition of spentwash :

The distillery spentwash used in the present investigation was obtained from the distillery unit of M/s Rajshree Sugars and Chemicals Ltd., (RSCL), Vaigai dam, Theni district. The spentwash was very much concentrated, reddish brown in colour with unpleasant odour of burnt sugars. The brown colour could be ascribed to the presence of melanoidin, the reaction products of sugaramine condensation (Mailard, 1912). The unpleasant odour, is due to the presence of skatole, indole and other sulphur compounds which are not effectively decomposed by yeast, or methane bacteria (Rajukkannu and Manickam, 1997; Thiyagarajan, 2001). The spentwash was highly acidic (pH 3.94 to 4.30), but loaded with large amounts of salts which reflected on very high EC (> 45 dSm^{-1}),Table 1. The total dissolved solids were also high in the spentwash revealing its possible salinity hazard. Being originated from plant sources, the spentwash contained considerable amounts of plant nutrients and organic matter. Among the major nutrients, K was found in larger proportions followed by N and P. A low SAR, resulting from small amounts of Na in the spentwash is unlikely to affect any sodicity hazard in soil. While no CO_3^{2-} was detected, very high concentrations of Cl^-, HCO_3^- and SO_4^{2-} were observed. The spentwash contained small amounts of micronutrients whose concentrations followed in the order of Fe > Mn > Zn > Cu. Considering the huge volume of nutrients in the distillery spentwash, it can be utilized as a cheap nutrient source and as an ameliorant for sodic soil reclamation under dryland and wet land conditions.A very high BOD, COD and other components like phenols, lignins, oil and greases in spentwash may lead to pollution of soil and water ecosystem. However, on the other hand, the spentwash is highly biodegradable as the ratio of COD and BOD is less than 2. The polluting effects of spentwash are mainly due to high concentration and readily decomposable organic matter. When it decomposes, obnoxious odours of H_2S would be emanating from sulfates, indole, skatole and from the dead yeast cells (Rajukkannu and Manickam, 1997). Presence of proteins, fulvic acid and humic acids further adds manurial value to the spentwash.

Soil reaction (pH) :

The pH of the sodic soil ranged from 7.65 to 9.46 during incubation (Table 2). The pH declined from 9.44 in control to 8.22, 8.00, and 7.75 for 55, 110 and 225 ml of spentwash application kg^{-1} soil, respectively. The pH measured immediately after spentwash application (Ist day) decreased significantly due to different levels and the pH increased gradually with the period of incubation from 1 to 60 days. The pH of the soil was higher (mean value of 8.42) on the 60th day of incubation when compared with the mean pH of 8.28 at the Ist day of spentwash application. One of the major reasons for such a drastic reduction in soil pH due to spentwash application might be due to the acidity resulting from the presence of various organic acids. (Dowd *et al*. 1994 and Rajukkannu *et al*. 1996. During the course of incubation, the pH of the soil raised slowly that can be attributed to the reaction of acidic spentwash with soil minerals dissolving large amounts of Ca, Al and Fe some of which undergo alkaline hydrolysis releasing OH^- ions into the soil solution and subsequently precipitate as new compounds.

Electrical conductivity (EC) :

The EC of the initial soil was 0.84 dSm^{-1}. Increasing rates of spentwash significantly increased the EC of the soil as reflected by the EC values of 0.82 dSm^{-1} in control and 11.22 dSm^{-1} at 225 ml spentwash kg^{-1} soil (Table 3). At all the stages of incubation, the increase in the EC with the increasing levels of spentwash was progressive and significant. A marked decline in EC was observed

Table 1 : Characteristics and composition of spentwash.

S. No.	Properties	Lagoon-1*	Lagoon-2*
A. Physical and chemical			
1.	Colour	Reddish brown	Reddish brown
2.	Odour	Unpleasant smell of burnt sugars	Unpleasant smell of burnt sugars
3.	Specific gravity (g/cm^3)	1.06	1.06
4.	Total suspended solids ($mg\ l^{-1}$)	61975.00	53816.00
5.	Total dissolved solids ($mg\ l^{-1}$)	79000.00	89166.00
6.	Total solids ($mg\ l^{-1}$)	140975.00	142983.00
7.	Total volatile solids ($mg\ l^{-1}$)	38250.00	44166.00
8.	pH	4.30	3.94
9.	EC (dSm^{-1})	45.20	48.00
10.	N ($mg\ l^{-1}$)	4200.00	4900.00
11.	P ($mg\ l^{-1}$)	3038.00	3217.00
12.	K ($mg\ l^{-1}$)	17475.00	18263.00
13.	Ca ($mg\ l^{-1}$)	7000.00	7000.00
14.	Mg ($mg\ l^{-1}$)	2100.00	3200.00
15.	Na ($mg\ l^{-1}$)	280.00	290.00
16.	Cl ($mg\ l^{-1}$)	42096.00	42835.00
17.	SO_4 ($mg\ l^{-1}$)	3240.00	3699.00
18.	CO_3 ($mg\ l^{-1}$)	Nil	Nil
19.	HCO_3 ($mg\ l^{-1}$)	3025.00	3058.00
20.	SAR	4.15	4.06
21.	SSP	1.04	1.01
22.	Potential Salinity ($mg\ l^{-1}$)	43716.00	44689.00
23.	Fe ($mg\ l^{-1}$)	25.90	26.20
24.	Mn ($mg\ l^{-1}$)	5.10	4.60
25.	Zn ($mg\ l^{-1}$)	8.50	8.60
26.	Cu ($mg\ l^{-1}$)	0.80	1.20
B. Organic components			
1.	BOD ($mg\ l^{-1}$)	96000.00	117333.00
2.	COD ($mg\ l^{-1}$)	134400.00	136466.00
3.	Organic carbon (%)	4.01	4.78
4.	Fulvic acid (%)	37.72	31.63
5.	Humic acid (%)	4.75	3.66
6.	Protein (%)	13.89	13.24
7.	Total phenols ($mg\ l^{-1}$)	58324.00	52310.00
8.	Lignins ($mg\ l^{-1}$)	5382.00	3705.00
9.	Total reducing sugars (%)	3.91	3.49
10.	Non reducing sugars (%)	2.53	2.15

* Mean of two replications

Table 2 : Influence of distillery spentwash on soil reaction (pH) (Mean of four replications)

Treatments	Days of incubation					
Spentwash levels	1	15	30	45	60	Mean
S_0 – control	9.42	9.45	9.42	9.43	9.46	9.44
S_1 – 55 ml kg^{-1} soil	8.15	8.24	8.23	8.25	8.25	8.22
S_2 – 110 ml kg^{-1} soil	7.90	7.98	7.98	8.05	8.08	8.00
S_3 – 225 ml kg^{-1} soil	7.65	7.69	7.70	7.82	7.90	7.75
Mean	8.28	8.34	8.33	8.39	8.42	

	S	D	S x D
SEd	0.03	0.02	0.05
CD (P = 0.05)	0.06	0.05	0.10

during the first 15 days of incubation (6.05 to 5.63 dSm^{-1}) and however, the decrease was insignificant at 30, 45 and 60 days after incubation (5.65, 5.65 and 5.66 dSm^{-1}) compared to initial EC (6.05 dSm^{-1}). The striking influence of spentwash in hiking the EC from that of the original soil could be noticed at all levels throughout the period of incubation. The EC increased progressively and significantly with increasing rates of spentwash application. Nearly 2.75 to 3.25 dSm^{-1} unit increase was observed for of spentwash in hiking the EC from that of the original soil could be noticed at all levels throughout the period of incubation. The EC increased progressively and significantly with increasing rates of spentwash application. Nearly 2.75 to 3.25 dSm^{-1} unit increase was observed for every 50 ml incremental addition of spentwash kg^{-1} soil . The salinity level remained below 4.0 dSm^{-1} for the lowest rate of spentwash (55 ml kg^{-1} soil) whereas it escalated to an EC of 11.2 dSm^{-1} for the highest rate of 225 ml spentwash kg^{-1} soil. Such an increase was quite expected as the spentwash had an inherent EC ranging from 45.2 to 48.0 dSm^{-1} due to heavy loads of salts. The changes in soil EC for different spentwash

Table 3 : Influence of distillery spentwash on soil electrical conductivity (dSm^{-1}) (Mean of four replications)

Treatments	Days of incubation					
Spentwash levels	1	15	30	45	60	Mean
S_0 – control	0.84	0.82	0.85	0.80	0.80	0.82
S_1 – 55 ml kg^{-1} soil	3.75	3.54	3.51	3.56	3.56	3.58
S_2 – 110 ml kg^{-1} soil	7.62	7.20	7.25	7.25	7.20	7.30
S_3 – 225 ml kg^{-1} soil	12.00	10.96	10.98	11.00	11.15	11.22
Mean	6.05	5.63	5.65	5.65	5.66	

	S	D	S x D
SEd	0.36	0.20	0.56
CD (P = 0.05)	0.72	NS	NS

Table 4 : Influence of distillery spentwash on free $CaCO_3$ content (%) (Mean of four replications)

Treatments	Days of incubation					
Spentwash levels	1	15	30	45	60	Mean
S_0 – control	2.42	2.35	2.26	2.20	2.28	2.30
S_1 – 55 ml kg^{-1} soil	2.10	1.96	1.75	1.62	1.55	1.80
S_2 – 110 ml kg^{-1} soil	1.95	1.72	1.60	1.48	1.40	1.63
S_3 – 225 ml kg^{-1} soil	1.72	1.60	1.52	1.32	1.35	1.50
Mean	2.05	1.91	1.78	1.66	1.58	

	S	D	S x D
SEd	0.03	0.02	0.05
CD (P = .05)	0.06	0.04	0.11

levels during the period of incubation was not significant.

Calcium carbonate content (free $CaCO_3$) :

The initial free $CaCO_3$ in the experimental soil was 2.42 per cent. The $CaCO_3$ content of the soil decreased significantly and gradually with the increasing doses of spentwash application (Table 4). The $CaCO_3$ content was 2.30 per cent in control and it decreased to 1.80, 1.63 and 1.50 per cent at spentwash application rates of 55, 110 and 225 ml spentwash kg^{-1} soil. The content of $CaCO_3$ at 1st days after incubation was the highest (2.05%) and gradually decreased with the rest of the incubation period to 1.58 per cent at 60th day of incubation. Further, it was observed from the interaction among the incubation period and treatment that the control (S_0) registered the highest value of $CaCO_3$ content (2.42%) at the 1st day of incubation and the lowest value of 1.32 per cent at 225 ml spentwash kg^{-1} soil at 45 days after spentwash application. The profound influence of spentwash in decreasing the $CaCO_3$ content of the non-saline sodic soil was very well brought out in the present study. As the rates of spentwash and $CaCO_3$ content were inversely related to each other, an appreciably lower concentration of 1.32 per cent was registered at 225 ml spentwash application kg^{-1} soil compared to 2.42 per cent in control. The acidic spentwash solubilise the insoluble $CaCO_3$ resulting in a significant decrease of the soil lime content. (Patil and Shinde, 1995).

Cation Exchange Capacity (CEC) :

TheCEC of the spentwash treated soil ranged between 27.6 and 28.3 c mol. (p^+) kg^{-1} as against the CEC of the control soil 25.5 c mol. (p^+) kg^{-1}. (Table 5).This increase might probably be due to the addition of higher organic matter and their decomposition products through spentwash. Such favourable changes in CEC may also be attributed to reduction in ESP consequent to the increase in soil organic carbon content.

Exchangeable Sodium Percentage :

The ESP of the soil decreased significantly due to application of different levels of spentwash. It decreased from 32.3 per cent in control to 15.4 per cent at 225 ml spentwash kg^{-1} soil on the 1st day and from 29.8 per cent to 9.7 per cent at 225 ml spentwash kg^{-1} soil on 60th day of incubation.(Table 5).The ESP also decreased significantly with the advancing period of incubation as reflected by the mean ESP values of 23.6 per cent on the 1st day and 16.7 per cent on the 60th day. Irrespective of spentwash levels, the soil ESP was brought down to < 15 at 60 days after incubation. Simple hydrolysis of native $CaCO_3$ released exchangeable Ca and increase in the supply of exchangeable K, Ca and Mg through spentwash addition might have facilitated the removal of exchangeable Na through Na through stochiometric reactions which in turn reduced the ESP of the soil. This mechanism which is operating in spentwash treated soil could be a very tangible reason for the reduction in soil ESP (Stewart and Wood, 1991). These observations indicated the profound effect of spentwash on the reclamation process of sodic soil.

Sodium Adsorption Ratio :

The SAR, an index of sodicity in soil was significantly influenced by the spentwash application. It decreased from 11.7 in control to 8.3 at 225 ml spentwash kg^{-1} soil application on the 1st day and from 10.2 in control to 6.5 untreated control to 6.5 at spentwash application

Table 5 : Cation Exchange Capacity [c mol (p^+) kg^{-1}], Exchangeable Sodium Percentage and Sodium Adsorption Ratio as influenced by spentwash (Mean of four replications)

Treatments	CEC			ESP			SAR		
	Days of incubation								
Spentwash levels	1	60	Mean	1	60	Mean	1	60	Mean
S_0 – control	25.5	25.6	25.5	32.3	29.8	31.0	11.7	10.2	11.0
S_1 – 55 ml kg^{-1} soil	26.6	28.5	27.6	24.7	13.9	19.3	9.8	7.9	8.9
S_2 – 110 ml kg^{-1} soil	26.9	27.1	27.0	22.0	13.3	17.7	8.6	7.2	7.8
S_3 – 225 ml kg^{-1} soil	27.8	28.8	28.3	15.4	9.7	12.6	8.3	6.5	7.4
Mean	26.8	27.4		23.6	16.7		9.6	7.9	
	S	D	S x D	S	D	S x D	S	D	S x D
SEd	1.0	0.7	1.4	0.8	0.6	1.2	0.4	0.3	0.6
CD (P = 0.05)	2.1	NS	NS	1.6	1.2	2.4	0.8	0.6	1.1

Table 6 : Influence of distillery spentwash on soil organic carbon content (%) (Mean of four replications)

Treatments	Days of incubation					
Spentwash levels	1	15	30	45	60	Mean
S_0 – control	0.24	0.28	0.30	0.30	0.32	0.29
S_1 – 55 ml kg^{-1} soil	0.45	0.42	0.50	0.54	0.62	0.51
S_2 – 110 ml kg^{-1} soil	0.56	0.58	0.64	0.67	0.69	0.62
S_3 – 225 ml kg^{-1} soil	0.70	0.64	0.72	0.75	0.76	0.70
Mean	0.49	0.48	0.55	0.57	0.61	

	S	D	S x D
SEd	0.02	0.03	0.06
CD (P = 0.05)	0.05	0.06	0.11

of 225 ml kg^{-1} soil indicating the effectiveness of spentwash in minimizing the sodicity of soil solution. Accordingly in the present study, the increase in the relative proportion of water soluble Ca^{2+} and Mg^{2+} might have appreciably lowered the SAR values in the spentwash applied non-saline sodic soil.

Organic carbon content (OC) :

Application of spentwash increased the organic carbon content of the high pH soil with increasing level of its application (Table 6). S_0 recorded the lowest value (0.29 per cent) while S_3 had the highest value(0.62 per cent). The organic carbon content of all the treatments was increased at 60 days after incubation when compared to frist day after incubation. The maximum organic carbon content (0.76 per cent) was recorded in the soil treated with 225 ml spentwash kg^{-1} soil at 60th day of incubation.An increase in organic carbon content was observed with effluent application during incubation and the increase was from 0.24 per cent in control to 0.70 per cent at 225 ml spentwash kg^{-1} soil. Addition of organic mater through the distillery effluent could possibly be a very tangible reason for this build up in organic carbon content of the soil. (Devarajan and Oblisamy,1996 and Mallika, 2001. The increase in organic carbon content with the period of incubation can be attributed to the continuous decomposition or microbial oxidation of the organic matter present in the soils treated with different rates of spentwash.

Spentwash is an acidic liquid, rich in organic carbon, Ca, Mg, S and K with considerable amounts of N, P and micronutrients. The composition of spentwash indicated the scope of utilizing it as an amendment for the reclamation of sodic soil and as a cheaper source of plant nutrients for enhancing the fertility status and organic matter content of the soils of our country. Application of spentwash @ 55,110 and 225 ml kg^{-1} soil were found equally effective in reducing the pH of air dried soil to = 8.3 during the incubation period of 60 days. Apropos to this, an increase in EC to the tune of 2.75 to 3.25 dSm^{-1} per 50 ml incremental addition of spentwash kg^{-1} soil was observed indicating the potential salinity of spentwash and consequently the buildup of salinity in soil. However, the EC of the soil treated with 125 m^3 spentwash ha^{-1} was below the critical limit while the higher rates of spentwash (250 and 500 m ha^{-1}) registered EC values > 6 dSm^{-1}.The ESP decreased from 32.3 to < 14 and SAR from 11.7 to < 8.0 for all the levels of spentwash. Further, the free $CaCO_3$ content of the soil was also solubilised due to the acidity of spentwash and reached a concentration of less than 2 per cent. The addition of organic matter through spentwash has enhanced the organic carbon content of the soil from 0.24 per cent to 0.62 per cent thus increasing the availability of nutrients to the soil.

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