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Investigation of plant nutrients availability in different sugar distillery spent wash by Inductive couple plasma membrane (ICPMS-AAS) for organic agriculture

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Abstract

The desire for - Cyclic Economy, Green and eco-friendly technologies and production methods - forces us to find new methods of waste minimization, waste recycling and reuse. Distillery spent wash could be a rich source of nutrients for plants. Present study was undertaken to analyse the elemental composition of four different sugar distillery spent wash in the Maharashtra State of India by ICPMS-AAS for its possible application as a source of plant nutrient for organic agriculture. Presence of sixteen elements were detected which were compared in the different distillery spent wash. It was observed that the samples involved varying amounts of essential elements which could be useful for plant growth with significant quantity of Fe, Mn, Sr, Al, K, Cr, Mo, Co, Se, Cu, and lower quantities of Ca, Pb, Ni, Mg. It was concluded that spent wash contained abundant quantity of micro and macro plant nutrients and can be used for organic agriculture.

Key words: Cyclic Economy, Organic Agriculture, Green chemistry, Plant nutrient, Inductive couple plasma membrane (ICPMS-AAS)

Introduction

India tops in production of sugar (typically cane sugar) in the world. Almost every state of India has Sugar producing factors. These sugar factories are in combination with the alcohol producing industrial plants which thus generate spent wash called as ‘Distillery Spent Wash (DSW)’ as their by-product / waste. Government of India’s efforts are directed towards using such alcohol produced (typically ethanol) as a fuel for automobiles by

blending it with Biodiesel or diesel. Maharashtra state of India is one of the leading producers of cane sugar and alcohol – which results in production of large amount of distillery spent wash (DSW) as a waste / by-product. Certain meaningful utilization of this distillery spent wash is needed or otherwise will result in accumulation of DSW near to the industry which is no good. In a Cyclic Economic (Three Principles: Reduce, Recycle, Reuse) / Green (Eco-Friendly) Technologies, the production process wastes are either reprocessed and used back again in the primary process itself or used for secondary applications. Example of the first could be – Purification of the textile industry waste water and again utilizing the purified water in the colouring process of the textile (i.e., in its primary process of production). Example of the later could be processing of the plastic waste to produce secondary products. It is known that distillery spent wash (DSW) contains different elements and chemicals which could be useful for plant growth if used in agriculture. It can even be considered as Organic Fertilizer for plants and vegetables. Realistic application of the distillery spent wash for agriculture application as a source of plant nutrients could serve two purposes: (1) making the production process greener (with reduced waste) and (2) moving towards Organic Agriculture. The quest for Organic Agriculture is increasing as people are becoming more aware of the drawbacks of the chemical fertilizers, pesticides, insecticides used in agriculture. However, in order to achieve the meaningful, large-scale use of distillery spent wash (DSW) in agriculture as a source of plant nutrients; it is important to study its composition, elements present, pH, and similar other characteristics – which thus became the focus of our present study.

Typically, literature search indicates that the distillery spent wash (DSW) is dark brown in colour, unpleasant odour, non-toxic, with high Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) and contains large quantity of soluble organic material and various elements / minerals. Spent wash is acidic, extreme amounts of soluble salts to be percolated from calcareous and presence of higher amounts of N, P, K and Ca as well as existence of growth agent's gibberellic acid and indole acetic acid into the spent wash (Sindhu S, et al 2007). Distillery spent wash is used in agriculture and develop and focuses methodology on 3R principle i.e., reduce, reuse, recycle (Cristiano E. Rodrigues Reis and Bo Hu 2017). Currently, various method used for recycling and reuse of distillery spent wash viz ferti-irigation, vermi-filtration, trans-esterification, microbial fuel cell, phyto-remedification, and microbial composting, recycling to fermentation streams, energy production, animal feed and sustainable agriculture (Vineet Kumar, Pankaj Chowdhary et al 2021). Effective and eco-friendly treatments methods have been applied on the spent wash which includes fungal, adsorption, electro-sorption, filtration, biological to avoid the environmental pollution load (Nusrat Ali, Sohail Ayub et al 2015). Application of chemical fertilizer and pesticides used inappropriately by farmer generate several human health problems, polluting our water, soil and air. Thus, the quest for Organic Agriculture is increasing (Nayana Sharma, Ritu Singhvi 2017).

The sugar distillery spent wash is a liquid waste obtained after production of alcohol. India is second largest producer of ethanol in Asia and fourth largest producer in the world. In India, ethanol market is one of the fastest

growing industries in the world (A. Muthusamy G. Kalpana 2017). More than 60 % of the total alcohol production in India is from three states Maharashtra, Uttar Pradesh, and Madhya Pradesh. One litre of alcohol production generated 10 - 15 litres of spent wash. Annually, 40 billion litres waste water generated from sugar industry distillery. In India, a total number of 290 distilleries with an installed capacity of about 3200 million litres are functioning.

In past, many researchers have studied and used distillery spent wash as source of plant micro -macro nutrients / fertilizer for crops. Use of distillery spent wash is observed to improve the soil fertility. Compared to synthetic inorganic fertilizers; DSW is cost efficient and easily available. With proper dilution, DSW can be used as a fertilizer along with the irrigation of crops (Karanam P, Joshi H 2010). The administration of DSW in controlled concentration is observed to be useful for plant germination, plant growth, yield, photosynthetic activities, improving the content of antioxidants and soil fertility (Muhammad Umair Hassan, Muhammad Aamer et. al. 2020). Application of spent wash improving physical and chemical properties of soil, fertility, microflora of soil, and water retaining capacity of the soil (Kamble, S.M., Dasar, G.V. and Gundlur, S.S. 2017). Application of distillery spent wash increased the crop yield of crop species sorghum, wheat, maize, sugarcane, cotton, groundnut, sunflower, soybean, sugar beet, potatoes and other vegetables, forage crops and tree crops. Diluted spent wash is recommended for mitotic cell division of early growth of the sugarcane genotypes which is also observed to increase the productivity of vegetables (Srivastava S, Jain R 2010, Chidankumar C. et al. 2009).

Many of technology and method using distillery spent wash used for composting of press mud. In India major use as making compost named as ‘treated press mud’ is produced by spraying spent wash on stacks of press mud formed value added organic manure for agriculture. Mostly, composting with press mud and vermiculture treatment manure used for sustainable agriculture (M. Baskar, A. Saravanan, et al 2013). Distillery spent wash combined with press mud, bagasse ash, plant leaves, sugarcane trash, cow dung and made valuable added fertilizer for increasing crop yield.

One of the major drawbacks of the earlier studies is that in most of the studies, the elemental composition and chemical composition was estimated by various chemical techniques with no direct proof by spectroscopic methods. Thus, we thought to use Inductive couple plasma membrane (ICPMS-AAS) for understanding the distillery spent wash.

Materials and Methods:

Study area and collection of samples:

The Sugar distillery spent wash (DSW) samples were collected from Maharashtra, India sugar mills. Four sugar distillery units selected - 2 from Pune district, 2 from Solapur district. Malegaon Sugar factory Distillery (District Pune), Someshwar Sugar factory Distillery (District Pune), Saswad-mali Sugar factory Distillery (District Solapur), Pandurang Sugar factory Distillery (District Solapur). Distillery Spent wash were collected in plastic container and labelled properly for laboratory analysis. Distillery Spent wash was filtered on filter paper No. 42 before using it for analysis.

Inductive couple plasma membrane (ICPMS-AAS):

Model No. - X SERIES II, Perkin Elmer model AAS 400, Make: Thermo Electron Corporation. Inductively coupled plasma mass spectrometry (ICP-MS) is a type of mass spectrometry which is capable of detecting metals and several non-metals at concentrations as low as parts per billion on non-interfered low-background isotopes. The plant nutrients macro micro element concentrations availability in different distillery spent wash were determined by ICPMS-AAS.

Procedure for sample digestion:

The analytical procedure adopted for distillery spent wash was briefly described as under. 5 ml of distillery spent wash sample measured and then added with 8 ml of nitic acid (HNO_3) and 2 ml pf hydrogen peroxide. Digest sample in Ethos microwave digestion system at 200 ^{0} C for 15 minutes. After that dilute sample at 50 ml with distilled water. 2 ml of the digested sample was diluted to 25 ml for analysis on ICP-MS, for analysis of K, Ca, Mg same sample run on atomic absorption spectroscopy (AAS).

Table (1): Physicochemical parameter of Sugar distillery Spent wash (DSW)

Sr.No	**Parameter**	**Symbol**	**Unit**	Malegaon Sugar factory Distillery **(DSW1)**	Someshwar Sugar factory Distillery **(DSW2)**	Saswad-mali Sugar factory Distillery **(DSW3)**	Pandurang Sugar factory Distillery **(DSW4)**
1	Colour	-	-	Dark brown	Dark brown	Dark brown	Dark brown
2	Odour	-	-	Unpleasant	Unpleasant	Unpleasant	Unpleasant
3	pH	-	-	9	4	3.96	3.83
4	Electrical conductivity	E.C	dSm	12.6	6.8	6.26	6.27
5	Potassium	K	%	1.80	1.96	1.05	0.93
6	Calcium	Ca	%	0.012	0.32	0.36	0.25
7	Magnesium	Mg	%	0.24	0.33	0.29	0.22
8	Boron	B	ppm	2.93	2.99	0.00	0.00
9	Aluminium	Al	ppm	2.95	3.12	9.68	1.23
10	Zinc	Zn	ppm	0.42	2.65	2.07	2.04
11	Manganese	Mn	ppm	3.05	7.29	35.98	3.05
12	Iron	Fe	ppm	11.96	73.31	204.38	100.20
13	Strontium	Sr	ppm	2.91	7.27	9.88	4.35
14	Nickel	Ni	ppm	0.41	0.71	0.70	0.41
15	Copper	Cu	ppb	34.88	24.75	798.13	302.00
16	Cobalt	Co	ppb	109.75	150.63	411.50	97.75
17	Selenium	Se	ppb	95.63	99.88	146.00	77.63
18	Chromium	Cr	ppb	224.9	295.0	1071.0	59.3
19	Molybdenum	Mo	ppb	175.38	382.25	297.75	247.13
20	Lead	Pb	ppb	0.042	0.139	0.069	0.158

Results and discussion:

A) Organoleptic and physical parameters

1) Colour (visual comparison):

The colour of spent wash was observed to be reddish brown which is known to be due to occurrence of caramelize sugar derivative obtained during distillation process known as melanoidin. Primary treated spent wash was reddish brown after diluted 50 % ,75 % goes to change brownish colour. Our observations are in accordance with the earlier reported results by Ramachandra et al. (Ramchandra and Pandey, P.K.,2000)

2) Odour:

Odour of distillery spent wash was unpleasant smell. Odour of spent wash was very strong, offensive and alcoholic in nature. Our observation is in accordance with earlier reports (Farid Ansari, Ajay K. et al 2012). High odour index of the distillery spent wash is originating from fermentation process. Anaerobic fermentation process produces volatile fatty acids, butyric and valeric acid (Ansari, Farid., Awasthi, K. et al 2010). The effluent was reddish brown in colour. Odour of samples was alcoholic in nature.

B) Physico-chemical characteristics of different distillery spent wash:

1) Variation of pH:

pH of different sugar distilleries was observed, pH value of DSW1, DSW2, DSW3, DSW4 were 9, 4, 3.96, 3.83 respectively. pH value of DSW1 was in alkaline range and DSW2, DSW3, DSW4 were in acidic range. Distillery spent wash is acidic and contains high levels of soluble salts. pH deviating from value 7 indicates that the samples should be neutralized for its pH before using them in agriculture. Directly using them will be harmful as they are either acidic or basic in nature.

2) Variation of Electrical conductivity (E. C.):

The values of different sugar distilleries spent wash were observed, it showed that, E.C of DSW1 DSW2, DSW3, DSW4 (12.61, 6.8, 6.26, 6.27) respectively. The E.C value observed in DSW1 (12.61dSm), which was highest from all DSW sample. Lower E.C observed in DSW3 (6.26 dSm).DSW2, DSW3, DSW4 observed nearly similar E.C value.

Micro and Macro nutrients:

This study reported that, the different DSW sample are different variation of plant nutrients availability. The physicochemical characteristics of spent wash were different pH, E.C, % of K, Ca, Mg and ppm of boron, aluminium, zinc, manganese, iron, nickel, copper, cobalt, selenium, chromium and molybdenum. Absence of boron in DSW3, DSW4 spent wash sample, but found to be significantly higher quantities of Cr, Mo, Co, Se, Cu, Fe, Mn, Sr, Al, K and lower quantities of Ca, Pb, Ni, Mg. The % of calcium, ppm of zinc, manganese, iron, nickel was in considerable decreases as compared to DSW2, DSW3, DSW4. Distillery spent wash contains high levels of soluble salts, higher amount of K followed by N and P. Significant amounts of Ca in spent wash used for reclaiming of sodic soils (Santiago Mahimairaja and Nanthi S. Bolan 2004). Heavy elements Cu, Co, Se, Cr, Mo is present in higher amount in all samples. Fe content is highest DSW3 compared to other factory spent

wash. Without proper treatment and direct use of distillery spent in agriculture causes heavy elements contamination of soil and crops (Sadiq Naveed, Abdur Rehim et al 2018). Pb is poisonous element present in small quantity as compared with other elements in samples so no chance of 'Lead poisoning'. Different distillery spent wash plant nutrient are different and varied due to production of alcohol process, water used in treatment, different kinds of raw materials such as sugarcane juice, sugarcane molasses. Variation of plant nutrient arises mainly from sugarcane, soil, environment, geographical area.

Conclusions:

All samples of DSW collected from four different industries in different parts of Maharashtra State of India are observed to be rich for plant nutrients with various elements were detected. Different sugar distillery spent wash were different chemical composition. Application of DSW can reduce the cost of fertilizers used in agriculture and minimize pollution load. Further study is underway to understand the actual effect of DSW on the growth of plants and seed germination.

Some of our observations / conclusive points are:

(1) The DSW should be appropriately diluted before being used in Agriculture (as a source of nutrients for plant growth).
(2) pH of the DSW needs to be adjusted to neutral before using in Agriculture. Strongly acidic DSW is no good for the plants.
(3) Various elements were detected in the DSW with varying concentration for the DSWs obtained from different industries. Heavy and poisonous metals were observed to be in very low quantity and can be omitted from consideration. It is safe to conclude here that such heavy (Cr, Mo, etc.) and poisonous (Pb) elements will not have any harmful effect on the growth of plants and vegetables and the humans who will be further consuming them.
(4) Certain DSW is observed to contain abundant quantity of certain element. Depending on the abundance of the element present in the DSW, plants and vegetable to which it can be useful can be easily identified. Example: DSW rich in Fe can be used for Fe containing fruit yielding plants or Fe containing vegetables.
(5) Educating farmer about the content of DSW and its proper method of using it should be done before actually using it in Agriculture.

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