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An Analysis on Physico-Chemical Characterization of Distillery Industrial Effluents

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Abstract – Effluent originating from distilleries known as spent wash leads to extensive water pollution. A study was conducted to know the quality of effluent generated from the distillery, for the purpose of proper treatment and dilution of effluent before discharge in water stream or on land. Physico-chemical characteristics of distillery effluent samples such as colour, odour, Total Solids, Total dissolved solids, Total Suspended Solids, pH, Electrical Conductivity, Total hardness, Calcium, Magnesium, Alkalinity, Chloride, Dissolved Oxygen, Biological Oxygen Demand, Chemical Oxygen Demand, Ammonical Nitrogen, Total Phosphorus, and Total Potassium were analyzed and it was observed that the characteristics of spent wash and PTDE (primary treated distillery effluent) have high load of chemical and organic pollutants. But when PTDE was diluted with 50% and 75% of water, all the values of physicochemical properties were decreased. The decrease in these values show that the toxicity of distillery effluent decreases with increasing dilution. Thus the characteristics of spent wash and PTDE do not allow its discharge into a water body; hence it requires treatment and dilution before discharge.

Effluents released from distillery industries are known for the damage they cause to the natural ecosystem if proper pretreatment procedure is not performed. A study is required to assess the physicochemical property of the effluent such as colour, odour, total dissolved solid (TDS), chemical oxygen demand (COD), pH, biochemical oxygen demand (BOD), electrical conductivity, and heavy metals which are considered as the mostly reported parameters to indicate the level of pollution from industrial effluents. The present study was conducted to investigate the physicochemical characteristic of one of the distillery effluent found in Addis Ababa, Ethiopia. In our investigation lower pH, higher temperature, higher concentration of chemical oxygen demand (COD) and biochemical oxygen demand (BOD) have been recorded.

Effluent originating from distilleries known as spent wash leads to extensive water pollution. Knowledge on the physico-chemical characteristics of distillery wastewater is essential in the design, operation, collection and treatment as well as disposal facilities for the effective management of environmental quality.

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INTRODUCTION

Recently great concern has been universally raised regarding environmental pollution as a side effect of rapid industrialization and subsequent urbanization. Today, the main concern with environmental pollution is with its impact on the health of the present generation and the coming ones. Our culture is completely river oriented and most of our important towns and urban areas are located on the bank of Major River. Unfortunately, untreated industrial wastes have been drained into the rivers and by river it is spreading over a large area. Therefore, it directly affects lives of flora and fauna not only in the industrial area but also in agricultural fields, river and river beds, thereby creating secondary source of pollution. Various industries have been continuously adding lot of waste water containing high level of nutrients, heavy metals and hazardous substances to the cultivable land.

However, effluents containing various metallic and nonmetallic elements act as nutrients but at the higher concentration they show toxic effects on seed germination and seedling growth, ultimately adversely affecting plant growth and yield in cultivated land . Moreover, deaths of domicile animals of such polluted water have been reported increasingly.

Industries as paper, textile, tannery, dye and distilleries are known for the considerable amount of wastewater they discharged to the environment

(Pawan et al. 2013). Distilleries releases enormous amount of waste water known as spent wash which is around 80 % of the raw material to the environment. The physicochemical characteristics of distillery effluent can be determined by the type of raw material utilized and treatment methods performed prior to the discharge of the effluent to the environment. Generally distillery effluents can be characterized by high level of biochemical oxygen demand (BOD), chemical oxygen demand (COD), phenolic compounds, sulphates, heavy metals, intense brown colour, lower pH, obnoxious odour, high electrical conductivity (EC) and high inorganic and organic salts.

Distillery effluent is most of the time disposed into the nearby water and land bodies. This effluent induces higher amount of foreign substances as heavy and toxic metals to the soil and water bodies which poses an adverse effect on the animals, plants and aquatic life.

Spent wash from distilleries is not only known for the environmental problem it causes. It is also known as a rich source of nutrients viz., potassium, sulphur, nitrogen, calssium, irron, magnisium, Zinc and biodegradable organic matter which playes significant role in inhancing soil fertility (Shyam and Swami, 2014). Therefore distilery effluents can be used for ferti-irrigation purpose and there are various reports supporting this fact. The result from different investigation showed the importance of distillery effluent in inhancing seed germination, seedling growth, shoot length, root length, nutritional quality, chlorophyll content and crop yield of agricaltural crops as: gram nut (Cicer arietinum), kidney bean (Phaseolus mungo) (Amit, 2013), ground nut (Arachis hypogaea L.), rice (Oryza sativa), gobi sarson (Brassica napus. L.), wheat (Triticum aestivum), okra (Abelmoschus esculentus), chickpea (Cicer arietinum L.) (Parvathi et al. 2014), finger millet (Eleusine coracana L.), mustard (Brassica juncea L.) (Vinod and Chopra, 2014), faba bean (Vicia faba L.), and sugarcane (Sacharum officinarum) to list some.

Utilization of distillery effluent for irrigation purpose must be done with great cares. This is because, distillery effluent imparts higher amount of heavy metals to the soil which will result in various environmental and health problems. Heavy metals can also affect the plant by inhibiting seed germination, seedling growth, nutrient availability and enzymatic activity. Accumulation of heavy metal in plant can reach animals through food chain and results in various health problems to the animals.

The physicochemical parameters are important in evaluating the level of toxicity of distillery effluents. Parameters such as color, turbidity, biochemical oxygen demand (BOD), chemical oxygen demand (COD), pH, Electrical conductivity, temperature, oxygen saturation, nitrogen, phosphorus, ion concentrations, organic contaminants and metal levels are mostly determined parameters. The main objective of the present study is also to evaluate the physicochemical characteristics of one of the distillery effluents.

Industries happen to be the major source of pollutants to the ecosystem. Different industries create a variety of wastewater pollutants; which are difficult and costly to treat. Wastewater characteristics and levels of pollutants vary significantly from industry to industry. The use of industrial waste as soil amendment has generated interest indecent time. The wastewater produced continuously could cater the needs of irrigated crops production of ethyl alcohol in distilleries based on sugarcane molasses constitutes a major industry in Asia and South America. The world's total annual production of alcohol from sugarcane molasses is more than 13 million m3. The aqueous distillery effluent stream known as spent wash is a dark brown highly organic effluent and is approximately 12-15 times by volume of product alcohol. The disposal of distillery spent wash is of serious concern due to its large volume and high biological oxygen demand (BOD) and chemical oxygen demand (COD). Due to high concentration of organic load, distillery spent wash is a potential source of renewable energy. The effluent does not contain any toxic heavy metals as it is a waste from plant materials. It contains high amount of nutrients such as nitrogen, phosphorous, potassium, sulphur and a large amount of micronutrients. The land application of distillery spent wash often benefits water pollution control and utilization for agricultural production. So it can be applied directly to the land as irrigation water as it helps in restoring and maintaining soil fertility, increasing soil micro flora, improving physical and chemical properties of soil leading to better water retaining capacity of the soil. The effluent is ideal for sugarcane, maize, wheat and rape seed production. It has been reported that wastewater from different industries produced continuously could cater the needs of irrigated crops. Thus, the distillery spent wash will not only prevent waste from being an environmental hazard but also served as an additional potential source of fertilizer for agricultural uses. The study was plain to evaluate the physico-chemical characterization of spent wash effluent and its dilution effect at different levels**.**

Various organic wastewaters that are known to cause serious problems may be accredited to distillery effluents, pulp and paper effluents, textile effluents, and tannery effluents. Among these, distillery wastewater is highly charged with organic matter. They pose a very serious threat to the environment because of the large volume of wastewater they generate which contains a significant amount of caramelized and recalcitrant compounds. These distillery wastewaters contain high level of COD and BOD, and low pH and are dark brown in colour, with unpleasant odour. At present, there are 285 distilleries in India that are producing 2.7 billion liters of alcohol and generating 40 billion liters of wastewaters annually. If these effluents are

discharged to water streams, the suspended solids present in the effluent would impart turbidity in water, reduce light penetration and impair the biological activity of aquatic life. Hence an economically viable and environmentally safe means of disposal is needed to handle such large volumes of waste water. Various studies dealing with the treatment of distillery wastewater are increasing rapidly. In recent years, there has been an attempt to conduct a survey and provide strategies to determine the role played by various distillery industries to this issue for improving and preserving the environment. It has been considered intelligent to investigate the condition of wastewater generated from a distillery industry. Hence, it is necessary to determine the physicochemical characteristics of any typical wastewater. This rapid analysis assists in assessing the quality of the wastewater for effective management and treatment strategies.

Distillery spent wash is perceived as one of the serious pollution problems of the countries producing alcohol from the fermentation and subsequent distillation of sugar cane molasses. The distillery spent wash is characterized as one of the caramelized and recalcitrant wastes containing extremely high COD, BOD, inorganic solids, color and low in pH.

In a developing country like India, distillery industries have become a major source of pollution, as 88% of its raw materials are converted into waste and discharged into the water bodies, causing water pollution. The disposal of large quantities of biodegradable waste without adequate treatment results in significant environmental pollution. This is the major source of aquatic and soil pollution. The discharge of wastewaters from distilleries is becoming increasingly restricted as pressures from environmental regulations increase and as awareness of the negative impacts of seasonal discharges of water containing high nutrient and organic loadings into water courses spreads.

At present, there are 285 distilleries in India that are producing 2.7 billion liters of alcohol and generating 40 billion liters of wastewaters annually. Distilleries, the alcohol producing industries, are one of the major polluting industries. A typical cane molasses based distillery generates 15 L of spent wash per litre of ethanol produced.

The post methanation distillery effluent (PME) produced from the treatment is characterized by high biological oxygen demand (BOD) and chemical oxygen demand (COD), intense brown colour and high salt levels apart from being rich in plant nutrients. Though the biomethanation of distillery effluent under anaerobic conditions brings down its BOD load from around 50,000 mg /l to 8,000-5,000 mg/l, due to their high organic load and salts, further treatment is still needed. If these effluents are discharged to water streams, the suspended solids present in the effluent would impart turbidity in water, reduce light penetration and impair biological activity of aquatic life. Hence an economically viable and environmentally safe means of disposal is needed to handle such large volumes of PME.

Analysis on physicochemical characteristics of distillery waste has been carried out, which stated that molasses is the most common raw material used in distilleries for bio-ethanol production. After alcohol distillation, huge volume of darkish coloured spent wash remains in the stills. The wastewater generally known as ‘spent wash’ is one of the most difficult waste products to dispose off, because of low pH and dark brown colour. It has high chemical oxygen demand (COD) and biological oxygen demand (BOD), causing pollution in the receiving water.

INDUSTRIAL EFFLUENTS AND THEIR IMPACT ON THE SOIL MICROFLORA

Industrial Effluents entering the water bodies is one of major sources of environmental toxicity. It not only affects the quality of drinking water but also has deleterious impact on the soil micro flora and aquatic ecosystems. Soil is the most favorable habitat for a wide range of microorganisms that includes bacteria, fungi, algae, viruses and protozoa. More than a million microorganisms represent the population per gram of then sample studied with bacteria and fungi being the prominent species prevalent. Industries keep on releasing effluents which is quite toxic whether its sugar mill or fertilizer industries, or chemical treatment given to the fields also cause problems for the survival of the soil micro flora Sugar processing requires hot water for a number of steps – such as water for imbibitions, raw sugar, remelting and various washings. Wastewater with varying levels of pollution load is generated at nearly all stages of sugar production. Relatively mild effluents from the mill house, containing oil, grease, and some sugar content, are generated from the lubricating and cooling systems, floor washings, the large quantity of water used for juice extraction, and some leakage and spill over. Washing the filter cloths used for sludge from the clarifier increases the suspended solids concentration and BOD of the wastewater. Combined with floor washings, which also add washing chemicals and more sugar, the process house effluents are considered more contaminated than effluents from the mill house. For mills that have an attached distillery, the numerous distillation stages produce a highly contaminated effluent, with BOD and COD concentrations of about 40,000 –100,000 mg/l, called stillage. In general, sugar mill effluents contain acidic and alkaline compounds, a significant concentration of suspended solids and a high BOD, COD, and sugar concentration.

Textile industry is one of the major sources of industrial effluents affecting the environment. The effluent which is untreated contains high concentrations of consumed metal dyes, phenol, aromatic amines etc.. Metal based coloured dyes and foaming chemicals used retard the biological activity due to reduction in the availability of light and cause metal toxicity to the aquatic and terrestrial habitats Water wastes released from the crude oil processing and petrochemical effluents are characterized by large amounts of hydrocarbons, crude oil products, polycyclic and aromatic hydrocarbons, metal derivatives, surface-active substances, sulphides and other chemicals. They lead to the accumulation of the toxic products in the waste-water and cause deleterious effects to the ecosystem reported the positive correlation between pollutants from the refinery and effects on the aquatic inhabitants and microflora.

CHARACTERIZATION OF UNTREATED AND ANAEROBICALLY TREATED DISTILLERY EFFLUENT

Distillery is an ancillary unit of sugar industry and uses cane molasses as raw material, which is a byproduct of sugarcane manufacturing. The distillery waste in large volume have a very high pollution potential due to the presence of large quantity of organic matters (Kaul et. al. 1993). All India Distilleries Association: has listed 212 distilleries which have an annual production of about 6500 million lit. of alcohol. Maximum number of distilleries are located in Maharashtra followed by Uttarparadesh (Srivastava and Pathak 1998).

Molasses based distilleries generate an average of 15 lit of wastewater called spent wash per litre of alcohol produced. This wastewater is characterized by high organic matter and dissolved solids, BOD, COD, low pH and dark brown color with a foul smell.

Because of the higher BOD and COD values distillery effluent create toxic conditions in the receiving stream by immediate depletion of oxygen. Its disposal results in massive destruction of aquatic flora and fauna and discoloration of streams. The offensive odour spreads over a few kilometers and results in serious public health hazard. Hence it becomes advisable to opt for safe and effective means of effluent treatment both as a practical necessity and as a social responsibility.

Discharge of effluents into fresh water streams deplete the DO content and causes higher mortality by interfering with respiratory metabolism.

METHODOLOGY

The sampling and analysis of various physico-chemical properties has been done to understand the composition of distillery effluent. The effluent samples were collected from Lord's distillery Ltd., Nandgaj, Ghazipur, U.P., India, samples were stored in dark place and the physico-chemical analysis of spent wash (distillery effluent), Primary treated distillery effluent (PTDE) and its dilution at different levels was studied i.e. its dilution with 50% and 75% of water were analysed for selected relevant physico-chemical parameters according to internationally accepted procedures and standard methods.

RESULTS -

The physicochemical properties of spent wash, PTDE (Primary Treated Distillery Effluent), PTDE diluted with 50% water and PTDE diluted with 75% of water was studied. Chemical composition such as colour, odour, Total Solids (TS), Total dissolved solids (TDS), Total Suspended Solids (TSS), pH, Electrical Conductivity (EC), Total hardness, Calcium(Ca), Magnesium (Mg), Alkalinity, Chloride (Cl), Dissolved Oxygen (D.O), Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Ammonical Nitrogen, Total Phosphorus, and Total Potassium were analysed and tabulated (Table 1). The data revealed great variation at different dilution levels of effluent. The spent wash and PTDE (Primary Treated Distillery Effluent) shows the higher values at all physicochemical parameters.

All the values decreased with increasing dilution whereas dissolved oxygen was increased.

Colour - The colour of spent wash was found dark brown. The colour of spent wash is suspected due to presence of a derivative of caramelized sugar formed during the distillation, termed melanoidin. The colour of PTDE (Primary Treated Distillery Effluent) was reddish brown while when it was diluted with 50% of water it turned brownish in colour and changed to light brown colour in PTDE diluted with 75% of water.

Odour - Odour of the distillery effluent was offensive. Odourous compounds from distillery waste water mainly consist of volatile fatty acids such as butyric and valeric acids that have a high odour index**.** Distillery has distinct organic compositions. Various anaerobic bacteria ferment these compounds and generate products such as volatile fatty acids for example glycerol is fermented into butyric acid by clostridium butyricum. The offensive odour of effluent was also reported. Odour of the PTDE, PTDE diluted with 50% of water and PTDE diluted with 75% of water was also offensive.

Total Solids - The total solids of spent wash were 42400.2 mg/l, but when it was treated, the value decreased. Total solids are the residues that include both dissolved solids and suspended solids. Distillery effluents contain huge amount of solids.

The total solids of the distillery effluent at different dilution levels decreased with dilution i.e. 28060.4 mg/l in PTDE, 16120.2 mg/l in PTDE diluted with 50%

of water and 10432.8 mg/l in PTDE diluted with 75% of water.

Total Dissolved Solids - The total dissolved solids of spent wash were 38200.2 mg/l. The total dissolved solids of the distillery effluent at different dilution levels were 22616.4 mg/l in PTDE, 12354.0 mg/l in PTDE diluted with 50% of water and 8010.8 mg/l in PTDE diluted with 75% of water.

Total Suspended Solids - The total suspended solids of spent wash were 4200.0 mg/l. The TSS of the distillery effluent at different dilution levels were 5444.0 mg/l in PTDE, 3766.0 mg/l in PTDE diluted with 50% of water and 2422.0 mg/l in PTDE diluted with 75% of water.

pH - The pH of the spent wash was acidic in nature i.e. 4.2 (the raw spent wash is acidic in nature and the pH values of distillery wastewaters range from 3.5 to 5.0). But when it was diluted with different dilution, it changed neutral to alkaline. The pH of distillery effluent at different dilution levels was 7.4, 7.6 and 7.7 at PTDE, PTDE diluted with 50% of water and PTDE diluted with 75% of water respectively. It shows the pH increases with dilution.

Electrical Conductivity - The electrical conductivity of the spent wash was 16450.8 (µmho/cm). The EC of distillery effluent at different dilution level was 14800.8, 8380.0 and 3476.2 (µmho/cm) at PTDE, PTDE diluted with 50% of water and PTDE diluted with 75% of water respectively. The electrical conductivity of distillery effluent was high but when it was diluted, value decreased with increased dilution.

Total Hardness - The total hardness of the spent wash was 2432.4 mg/l. The term total hardness indicates the concentration of calcium and magnesium ions. The total hardness of the effluent at different dilution level was 2060.8 mg/l, 1354.2 mg/l and 940.2 mg/l observed at PTDE, PTDE diluted with 50% of water and PTDE diluted with 75% of water respectively. The hardness was also higher in spent wash and decreased with increasing dilution.

Calcium - The calcium of the spent wash was 2070.0 mg/l. The calcium content of distillery effluent at different dilution level was 872.0 mg/l, 610.2 mg/l and 422.4 mg/l observed at PTDE, PTDE diluted with 50% of water and PTDE diluted with 75% of water respectively.

Magnesium - The magnesium of the spent wash was 2260.5 mg/l. The magnesium content of distillery effluent at different dilution levels was 1742.0 mg/l, 992.0 mg/l and 684.6 mg/l at PTDE, PTDE diluted with 50% of water and PTDE diluted with 75% of water respectively.

Alkalinity - The alkalinity of the spent wash was 2864.5 mg/l. The alkalinity of distillery effluent at different dilution levels was 3680.4 mg/l, 1880.0 mg/l and 1260.5 mg/l at PTDE, PTDE diluted with 50% of water and PTDE diluted with 75% of water respectively.

Chloride - The chloride of the spent wash was 8530.2 mg/l. The chloride content of distillery effluent at different dilution levels was 5352.6 mg/l, 2362.4 mg/l and 1464.4 mg/l at PTDE, PTDE diluted with 50% of water and PTDE diluted with 75% of water respectively.

Dissolve Oxygen - The D.O. was nil in spent wash and partially treated distillery effluent (PTDE) and the value was increased to 2.6 mg/l when PTDE was diluted with 50% of water, and 3.6 mg/l when PTDE diluted with 75% of water. The value of DO was increased with increasing dilution.

PARAMETERS	SPENT WASH	PTDE (Primary Treated Distillery Effluent)	PTDE diluted with 50% water	PTDE diluted with 75% water
Colour	Dark brown	Reddish brown	Brown	Light brown
Odour	Unpleasant	Offensive	Offensive	Offensive
Total solids	42400.2 ± 6.4	28060.4 ±16.0	16120.2 ±8.0	10432.8 ±12.4
Total Dissolve solids	38200.2 ± 4.8	22616.4 ±32.0	12354.0 ±10.0	8010.8 ±14.6
Total suspended solids	4200.0 ± 0.0	5444.0 ±0.0	3766.0 ±0.0	2422.0 ±0.0
pH	4.2 ± 1.2	7.4 ±0.8	7.6 ±0.6	7.7 ±1.4
EC (µmho/cm)	16450.8 ± 8.2	14800.2 ±12.4	8380.6 ±14.8	3476.8 ±16.4
Total Hardness	2432.4 ± 5.4	2060.8 ±5.6	1354.2 ±6.3	940.2 ±8.2
Calcium	2070.0 ± 2.6	872.0 ±6.2	610.2 ±4.0	422.4 ±6.2
Magnesium	2260.5 ± 6.7	1742.0 ±8.0	992.0 ±8.3	684.6 ±8.8
Alkalinity	2864.5 ± 8.0	3680.4 ±12.0	1880.0 ±10.0	1260.5 ±12.1
Chloride	8530.2 ± 8.3	5352.6 ±12.2	2362.4 ±6.0	1464.4±14.0
Dissolve Oxygen	Nil	Nil	2.6 ±0.4	3.6 ±1.3
Biological Oxygen Demand	32300.8 ± 10.8	14824.2 ±12.0	6890.5 ±16.2	3240.8 ±12.0
Chemical oxygen Demand	57164.6 ± 12.9	32030.2 ±16.2	11448.6 ±16.2	4254.8 ±14.5
Ammonical Nitrogen	1254.4 ± 2.4	714.2 ±12.2	412.3 ±6.4	286.6 ±8.0
Total Phosphorus	44.4 ± 5.6	32. 8 ±3.5	22.4 ±2.3	12.8 ±1.3
Total Potassium	7440.2 ± 3.8	5360.8 ±14.4	2854.2 ±8.2	1482.0 ±10.6

Table 1: Physicochemical characteristics of spent wash (Distillery effluent) and it dilution at different levels.

CONCLUSION

The distillery spent wash is a nutrient rich liquid organic waste obtained from molasses based distillery industries after and before Methanation process. The spent wash, being loaded with organic compounds could bring remarkable changes on the biological properties of soils and thus influences the fertility of soil significantly. Lower concentration of spent wash can be used to agricultural uses for safe metal concentration loading on arable land.

India is a developing country where small scale industrial units mainly in textile industry form a major part and effluent treatments are not taken care of. The costs of water treatment add to woes of the ailing smaller units. Hence, the values pH, TSS, TDS, BOD and COD are above the permissible limits. These effluents have deleterious effects on the soil sample collected from the site of effluent discharge.

The study reveals that the physicochemical characteristics of spent wash and PTDE (primary treated distillery effluent) have high load of pollutants. The effluent was reddish brown in colour. Odour of samples was alcoholic in nature. It is one of the most complex and cumbersome waste having very high value of solids, electrical conductivity, hardness, calcium and magnesium compounds, chlorides, BOD and COD content and highly acidic pH, while D.O. was found Nil and contains high organic load of nutrient elements such as nitrogen, potassium and phosphorus. When PTDE was diluted with 50% and 75% of water, all the values of physicochemical properties were decreased. The decrease in these values show that the toxicity of distillery effluent decreases with increasing dilution. Thus the characteristics of spent wash and PTDE do not allow its discharge into a water body; hence it requires treatment and dilution before discharge.

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