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COMPARATIVE STUDY OF 'BOD', 'DO' AND pH OF DISTILLERY TREATED AND UNTREATED WASTE WATER

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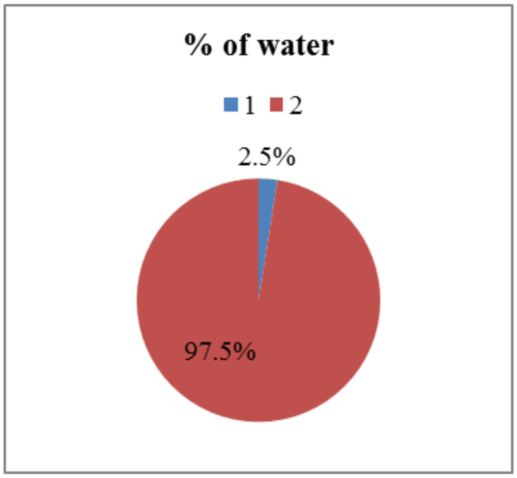
Abstract- Industrial processes create a variety of wastewater pollutants; which are difficult and costly to treat. The present study is under taken to assess the level of physiochemical parameters of the distillery spent wash. These parameters will compare with Bureau of Indian Standards. Untreated effluent is found to have high contents of BOD, and low contents of DO. According to the permissible limit suggested the Bureau of Indian Standards the untreated effluents is toxic to plant so it is not permissible for irrigation. The results reflect that the treated effluents are not highly polluted and they satisfy the Bureau of Indian Standards values and therefore can be used for irrigation purposes.It is one of the most complex, and strongest organic industrial effluent, having extremely high BOD values. Because of the high concentration of organic load. The paper reviews the status of BOD, DO and pH values before and after treatment of the distillery wastewater.

Index Terms- Distillery spent wash, BOD, DO and pH.

I. INTRODUCTION

Water is one of the most important compounds required for every existing of life. Adequate supply of fresh and clean drinking water is a basic need for all human beings on the earth, yet it has been observed that millions of people worldwide are deprived of this. Without clean water neither human nor the environment, which sustain them, can survive. Chemically it is a compound of two hydrogen atoms and one atom of oxygen. About 97.5% of world's water occurs as salt water, of the remaining 2.5%, two third occurs as snow and ice in the polar and alpine region so only about 1% of global water occurs as liquid fresh water. Groundwater is the underground water that occurs in the saturated zone of variable thickness and depth, below the earth's surface. More than 98% of fresh water present on the earth surface is in the form of ground water while streams, lake and rivers hold only 2% of the total available water therefore ground water is the most valuable natural resource.The demand for water has increased over the year and this has led to water scarcity in many parts of the world. The situation is aggravated by the problem of water pollution or contamination. Resent study have shown that groundwater is highly susceptible to pollution from natural as well as anthropogenic activities such as municipality sewage, industrial effluent, and agricultural field run off and leaching, landfills refuse dumps, septic tanks and improper collection of solid wastes. Quality of ground water is for important like its quantity. When we talk of the quality of ground water, it means some



Series 1: Drinking water on the Earth
Series 2: Nondrinking water
Fig 1 Total global water content [45]

peculiar characteristics of water in relation to a particular use.In safe water and inadequate sanitation is the world's leading cause of human illness. Disease and death are directly attributable to the lack of these essentials. Safe drinking water is vital human needs for health and efficiency. Determination of physical chemical bacteriological and heavy metals characteristics of water is essential for assessing the suitability of water for drinking, irrigation and industrial uses. Various standards has been laid down by various agencies such as the World Health Organization (WHO), the U.S Environmental Protection Agency (USEPA), the Bureau of Indian standards (BIS) & the Indian Council of Medical Research (ICMR) etc for determining the quality of water for various uses. Any physical chemical and biological change in water quality that adversely affects living organism or make water unsuitable for desired use can be considered pollution.According to the Natural Excessive use of pesticide and chemical fertilizers in farms aggravates the problem. India produces 11 million tones of fertilizer every year and much of it ultimately percolates down to the ground water sources and contaminates it.

Also Distilleries industries are one of the most polluting industries. In India there are about 579 sugar mills and 295 distilleries with a total installed capacity of 3198 million litres per annum and a yearly production of 1587 million litres alcohol. Alcohol is produced from molasses by two type of fermentation processes, Praj type and Alfa Laval distillation. In Praj type one litres alcohol produced about 12-15 litres of spent wash where as in the Alfa Laval continuous fermentation and distillation process only 7-8 litres of waste water per litres of alcohol is produced. The effluent coming from distillery industry is highly polluted which when seeps into the ground ultimately contaminated the ground water. [43]

1.1 Pollution And Toxicity Profile Of Distillery Effluent

The production and characteristics of spent wash are highly variable and dependent on feed stocks and various aspects of the ethanol production process. Wash water used to clean the fermenters, cooling water blow down, and boiler water blow down further contributes to its variability, [8]. In a distillery, sources of wastewater are stillage, fermenter and condenser cooling water and fermenter wastewater. The liquid residues during the industrial phase of the production of alcohol are liquor,

1.2 General Physico-Chemical Characteristics

Parameter	Range
Colour	Dark brown
Odour	Unpleasant burnt sugar
pH	3.8–4.4
Total solids (mg/L)	60000–90000
TSS (mg/L)	2000–14000
TDS(mg/L)	58000–76000
TVS (mg/L)	45000–65000
COD (mg/L)	70000–98000
BOD (mg/L)	45000–60000
Total nitrogen as N (mg/L)	1000–1200
Potash as K2O (mg/L)	5000–12000
Phosphate as PO4 (mg/L)	500–1500
Sodium as Na (mg/L)	150–200
Chlorides as Cl (mg/L)	5000–8000
Sulfates as SO4 (mg/L)	2000–5000
Acidity as CaCO3 (mg/L)	8000–16000

Typical characteristics of distillery spent wash, [27]

Schematic Of Alcohol Manufacturing Process:

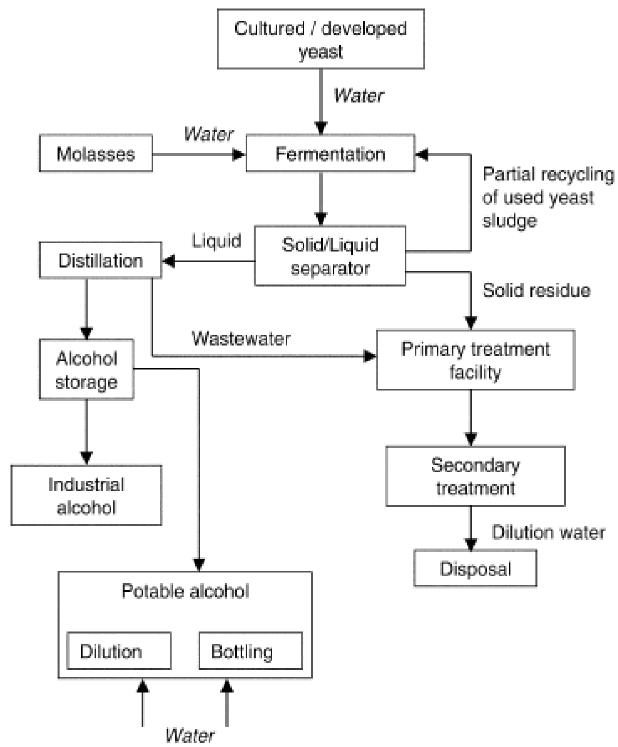


Fig. 2Manufacturing process of alcohols

sugarcane washing water, water from the condensers and from the cleaning of the equipment, apart from other residual water. This extract is extremely polluting as it contains approximately 5% organic material and fertilizers such as potassium, phosphorus and nitrogen. The amount of water used in this process is large, generating a high level of liquid residues, [6]. The MSW is a potential water pollutant in two ways. First, the highly coloured nature of MSW can block out sunlight from rivers and streams, thus reducing oxygenation of the water by photosynthesis and hence becomes detrimental to aquatic life. Secondly, it has a high pollution load which would result in eutrophication of contaminated water courses, [11]. Due to the presence of putriciable organics like skatole, indole and other sulphur compounds, the MSW that is disposed in canals or rivers produces obnoxious smell. Undiluted effluent has toxic effect on fishesand other aquatic organisms. Spent wash also leads to significant levels of soil pollutionand acidification in the cases of inappropriate land discharge.It is reported to inhibit seed germination, reducesoil alkalinity, and cause soil manganese deficiency and damageagricultural crops [1] - [18]. However, effect of distillery effluenton seed germination is governed by its concentration and iscrop-specific. In a study by Ramanathe germinationpercent in five crops decreased with increase in concentrationof the effluent [30]. The germination was inhibited inall the five crops studied with concentration exceeding 50%.At the same time, organic wastes contained in distilleryeffluent are valuable source of plant nutrients especially N, P, K and organic substrates if properly utilized [29]. For instance, distillery effluent in combination with bio amendments such as farm yard manure, rice husk and Brassica residues was used to improve the properties of sodic soil [18]. The use of fungi for bioconversion of distillery waste into microbial biomassor some useful metabolites have been recently reviewed by Friedrich. [12].

II. Available Technologies

2.1 Traditional Treatment Practices

Most of the wastewaters from different distillery sources were historically discharged directly into the soil or in ground water. Reich proposed one of the first treatment systems; a continuous integrated method to concentrate the stillage by fermentation, where the fermenter discharge was centrifuged and the yeast that was not recycled was drum-dried for use as an animal feed [31]. The stillage was concentrated to 70 to 80% solids and then neutralised with potassium carbonate (K_2CO_3). The concentrated, neutralised wastewater was passed through low-temperature carbonising retorts and activated at 870ºC, and the resultant carbonUnderwent aqueous extraction to produce potash fertiliser (potassium oxide (K2O)), potash liquor and char. A decade later, Montanani reported on the slightly more developed Tibrocal system, in which stillage was neutralised with lime [calcium oxide (CaO) or calcium hydroxide ($Ca(OH)_2$)] and then evaporated in 10 cm shallow containers, again for use as a fertiliser [24]. Other similar schemes were proposed by Chakrabarty and Yamauchi With the difference that crystallised potassium sulphate was produced instead of potassium oxide. [7]- [42]. In Europe, distillery wastewater was incinerated, normally yielding 34.7% of potash fertiliser and 2.2% phosphorus oxide (or ceramic oxide (P_2O_5) [33]. Another method was distillery wastewater concentration to 30 to 40° Brix, followed By spray drying and combustion at 700ºC, with the resultant ash being collected at the column base [15]. Similar methods were used with small variations, such as concentration of the stillage to 60% solids and spray drying into fuel gases, [10]. Tartrate removal has also been used as pre-treatment step [38]. Fluidised bed combustion of stillage, followed by heat recovery, has also been suggested [19]. However, scale formation was reported as a problem in some of the incineration and evaporation schemes, and the energy costs were prohibitive. Jackman reported on Brazilian efforts to reduce scaling and to raise the ash fusion temperature by adding other chemicals. [16] The French practice was to concentrate the stillage to 60% solids and then use it as a fertiliser at an application rate of 2.5 to 3.0 tonnes per hectare [20]. Monteiro considered this method uneconomical in the Brazilian context. [25]. the extraction of specific chemicals from wine distillery wastewater for sale as by-products has been conducted to offset the costs of wastewater treatment and to improve subsequent treatment and disposal [44]. Gypsum ($CaSO_4.2H_2O$) was recovered by the addition of seed crystals to the stillage at 80ºC and stirring at 22 to 25 rpm for 60 minutes. This alleviated the problem of gypsum precipitation in cases where stillage was to be used for fodder yeast growth. Potassium and its double salt ($K_2SO_4.5CaSO_4.H_2O$) can also be removed from wastewater concentrated to 30 to 60ºBrix [17]. It is found that stillage concentrated to 60 to 80º Brix formed coagulate when soluble phosphate was added and the temperature was increased to 105 to 120ºC [2]. The coagulate was then dried further and used as a fertiliser or ruminant fodder. Dubey stated that glycerol and germ oil were other chemicals that could be recovered from distillery wastewaters, but, even as late as 1980, distillery wastewater or stillage was still usually just evaporated to provide animal feed or fertiliser, or incinerated for the possible recovery of the potash [35].

2.2 Current Treatment and Disposal Options

More recent wine distillery wastewater treatment includes methods to remove recalcitrant compounds by physicochemical processes using distillery waste water and biologically-treated distillery wastewater [28]. In one case example, the physicochemical treatment of biologically-treated wastewater using conventional coagulant iron pickling wastewater supplemented with coagulant aid generated an effluent with COD in the range 940 to 1780 mg/L and a BOD of 25 to 30 mg/L. During this study, the colour of the treated wastewater was in the range of 580 to 1100 platinum cobalt units. It was recommended that the waste sludge from this industry be utilized as a substitute for conventional coagulants. Wastewater generated after chemical coagulation could be further treated efficiently by using 8 g/L of activated carbon with a contact time of 45 min to reduce residual COD to <250 mg/L to meet discharge limits [28]. Anodised graphite anodes were found to be suitable for the treatment of wine distillery wastewater, especially in the presence of supporting electrolytes such as sodium halide, or sodium chloride, which was found to be the most effective in the degradation of polyphenols [22]. Later a combination of the Fenton coagulation/ flocculation process (using H_2O_2/Fe_{2+}) for the treatment of wine distillery wastewaters obtained a 74% reduction in COD under optimized conditions [3]. The worldwide scarcity of water is a strong incentive for recovering clean water for reuse from wastewaters. Nataraj investigated the treatment of distillery spent wash by removing the colour and the contaminants using a combination of NF and RO processes [26]. Due to the high fluxes obtained, significant rejection rates of total dissolved solids (TDS), COD, potassium and chloride concentrations were achieved. The absence of heat energy requirements in this application. And the high rate of mass transfer generated by RO showed that a large amount of clean water could be permeated economically instead of being vaporized by energy-intensive evaporation Processes or steam distillation using tall towers. Water reclaimed by NF and RO is suitable for use in both municipal and industrial applications. Chemical oxygen demand was considerably reduced in distillery wastewaters in India in order to reduce the cost of wastewater disposal. This process emphasized the recovery and recycling of valuable chemicals contained in the wastewaters [26]. Some methods of treatment of wine distillery waste water result in single cell production, the production of organic acids for sale in the industrial market, and the production of viable biological products, including enzymes, astaxanthia, plant hormones and biopolymers such as chitosan [41]. Glycerol recovery, first suggested in 1974, was finally achieved towards the end of the 20th century by concentrating wastewater to 60% solids, followed by the addition of quicklime (calcium oxide (CaO)) and ethanol, which led to the precipitation of 90% of the glycerol that was present. Germ oil was obtained by heating distillery wastewater, centrifuging at 6000 g and extracting the oil solvent from the lightest fraction. As with the generation of fertilizer for direct land application, the economics of any treatment method rely heavily on the financial value that can be assigned to the resultant product. The pre-treatment of wine distillery waste water with ozone improves its kinetic behavior during anaerobic digestion, but at the same time decreases COD removal efficiencies [4] - [23]. Martin investigated the ozonation of vinasse in trying to reduce COD. [23]. Vinasse is known to be chemically very complex because of the high content of polyphenols, which delay biological processes such as anaerobic digestion. As a result, ozonation is seen as a desirable chemical pre-treatment prior to biological treatment because it is capable of converting the inhibitory and refractory compounds into simpler, low molecular weight compounds that are more readily degradable by microorganisms. Ozonation of aromatic compounds usually increases their biodegradability. However, in many cases the chemical pre-treatment used to make the waste biodegradable diminishes the COD of the wastewater, although intermediate compounds of higher microbial toxicity can be generated, depending on the type of ozonation used as pre-treatment [23]. In such cases, an alternative chemical oxidant has been used, and the treatment of wine distillery wastewater in a continuous reactor using a combination of ozonation and aerobic degradation in activated sludge systems has also been investigated [4]. In this combined system, oxidation by ozone achieved a reduction in the organic substrate concentration of 4.4 to 18%, while removal of the content of phenol compounds in the range of 50 to 60% was achieved. Aerobic degradation of these vinasses by activated sludge in experiments using varying hydraulic retention time (HRT) and substrate concentration provided organic substrate removal in the range of 12 to 60% [4]. Ozonation of this aerobically pre-treated vinasse led to an increase in COD removal efficiency from 16 to 21.5%, as well as higher rate constants [4]. Schafer later applied membrane filtration with concomitant chemical treatment in the management of wastewaters containing natural organic problems [34]. COD removal efficiencies were improved in aerobically pre-treated and then ozonated wastewaters [4].

III. Experimental View

3.1 Preparation of bagasse activated carbon (BAC):

Bagasse are collected from sugar industry and dried in oven at 110oC followed by sieving with mesh of pore size 425 . The sieved particles were washed several times with water and dried at 110oC for 6 hours in hot air oven to remove all the moisture content. The dried bagasse was then treated in combination with concentrated H2SO4and H3PO4in ratio of1:1 by volume, as activating agent to produce activated carbon. The sample was then washed with distilled water and soaked in 1% sodium carbonate solution for about 8 hours. The washing of sample with distilled water was continued until the pH of wash water turned to neutral. The samples were dried in hot air oven at 110oC for 24 hours. The final adsorbent are stored in airtight containers before using for adsorption studies. High moisture content is not desirable as it dilutes the adsorption capacity of the activated carbon and thus, larger dosages would be required. High ash content is not desirable as ash is the residue that remains when the carbonaceous material is burned off, the ash content indicates the inorganic constituents (mainly minerals such as silica, aluminum, iron, magnesium and calcium), associated with the carbon sample. These metals might leach from the activated carbon during adsorption and affect their performance adversely by competitive adsorption with the adsorbate. Hence, the prepared BAC was analyzed for pH, moisture content, conductivity, volatile matter content and ash content.

3.2 Dissolved Oxygen

The various gases which may get dissolved in water due to its contact with atmosphere or the ground surface may be nitrogen, methane, hydrogen sulphide, carbon di oxide and oxygen. The concentration of oxygen gas in river water is important. Oxygen gas is generally absorbed by water from the atmosphere; Algae and other tiny plant life of water also give oxygen to the water, but are being consumed by unstable organic matter for their oxidation. Hence, if the oxygen present in water is found to be less than its saturation level, it indicates presence of organic matter and consequently making the water suspicious.Dissolved oxygen is required for the respiration of aerobic microorganisms as well as all other aerobic life forms. However oxygen is slightly soluble in water. The rate of biochemical reactions that uses oxygen levels tends to be more critical in summer because the stream flows are usually lower and thus the total quantity of oxygen available is also lower. The presence of dissolved oxygen in wastewater is desirable because it prevents the formation of noxious odors.The presence of oxygen in water in dissolved form is necessary to keep it fresh and sparkling. Dissolved oxygen is also important to aquatic life because detrimental effect can occur when DO levels drop below 4-5 mg/L, depending upon the aquatic species. Oxygen levels that remain below 1-2 mg/L for few hours can result in fish kills.

3.3 Hydrogen Ion Concentration (pH):

The pH value of water is measure of its alkalinity or acidity. More accuracy sated the pH is a measure of the hydrogen ion concentration in water. Mathematically this is the logarithm to the base 10 of reciprocal of the hydrogen ion concentration of pure water. Thus a pH value of 7 indicates neutral solution, neither alkaline nor acidic. A pH less than 7 indicates an acidic solution indicates the presence of carbonate of calcium and magnesium and a pH value of 8.5 or above usually indicates appreciable exchargeable solution.

3.4 Biological Oxygen Demand

The extent of oxygen consumed by the organic matter present in water sample is known as Biochemical Oxygen demand (BOD). The BOD of raw water will indicate the extent of organic matter present in the water. If sufficient oxygen is present in water, the useful aerobic bacteria production will flourish and cause the biological decomposition of waste and organic matter, thereby reducing the carbonaceous material from the water. The amount of oxygen required in the process until oxidation gets completed is known as BOD. Polluted waters will continue to absorb oxygen for many months, till the oxidation gets completed and it is not practically possible to determine this ultimate oxygen demand. Hence the BOD of water during the first five days at 20^0C. The dissolved oxygen is measured after the period of incubation. The difference between the original oxygen content and the residual oxygen content will indicate the oxygen consumed by the water sample in five days. If BOD of water is zero it means that no oxygen is required and thus no organic matter is present. The extent of pollution of sewage and other industrial wastewater is also measured by determining the values of their BOD.

3.5 Reagents Used

Ferrous Ammonia Sulphate (FAS): It was prepared according to the standard method by adding to about 9.80 gram FAS and 5 ml H_2SO_4 in 250 ml distilled water.

Sulphuric Acid : It was prepared by adding 2.75 gram of and 272 ml of H_2SO_4 in 500 ml distilled water Then it was allowed to stand for one day to dissolve $AgSO_4$.

Potassium Dichromate ($K_2CR_2O_7$): It was prepared by dissolving 16.65 gram of $HgSO_4$, 83.5 ml H_2SO_4 and 2.45 gram $K_2CR_2O_7$ in 500 ml distilled water.

Phosphate Buffer: It was prepared by adding 8.5 gram pot. Hydrogen phosphate, 21.75 gram Di Pot. Hydrogen phosphate, 33.4 gram di sodium hydrogen phosphate and 1.7 gram Ammonium chlorides dissolved in 500 ml distilled water and then dilute with 1litre distilled water.

Magnesium Sulphate: It was prepared by adding 22.5 gram Magnesium sulfate in 1 liter distilled water.

Ferric Chloride (FECL): It was prepared by adding 2 gram FECl 1 liter distilled water.

Calcium Chloride: It was prepared by adding 27.5 gram calcium chloride in 1 liter distilled water.

MagnousSulphate ($MnSO_4$): It was prepared by adding 364 gram $MnSO_4$ in 1 liter distilled water.

Alkali Azide: It was prepared by adding 125 gram NAOH Sodium hydrogen pallets, 37.5 gram potassium Iodide and 2.5 gram Sodium Azaid (NAH_3) in 250 ml distilled water.

Sodium Thiosulphate of 0.025 Normality : It was prepared by adding 6.205 gram in 1 liter distilled water.

Starch Indicator: It was prepared by adding 2 gram starch powder and 0.2 gram salicylic acid in 100 ml distilled water.

Potassium Chromate: It was prepared by adding 12.5 gram Potassium Chromate in 100 ml distilled water and then after 12 hours filter the solution and add 250 ml distilled water.

3.6 Observation Table

Table 1

S.N	Parameter	Treated Effluent	BIS standards
1	Colour	Light Brown	-
2	Temperature	38°C	-
3	pH	6.8	6.5-9.0
4	DO	2.3 mg/l	4-6 mg/l
5	BOD	38000 mg/l	500000 mg/l

Table 2

S.N	Parameter	Unreated Effluent	BIS standards
1	Colour	Light Brown	-
2	Temperature	40°C	-
3	pH	4.6	6.5-9.0
4	DO	1.3 mg/l	4-6 mg/l
5	BOD	35000 mg/l	500000 mg/l

The Physico-chemical parameters of treated and untreated effluent viz. BIS standards

3.6.1 DO in effluent before treatment and after treatment

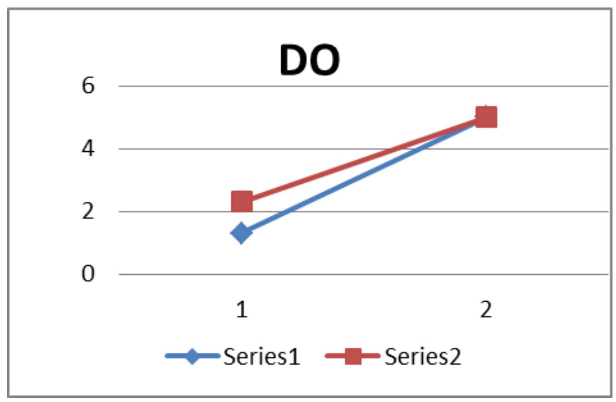


Fig. 3 Series 1: DO of untreated effluent

Series 2: DO of treated effluent

3.6.2 BOD in effluent before treatment and after treatment

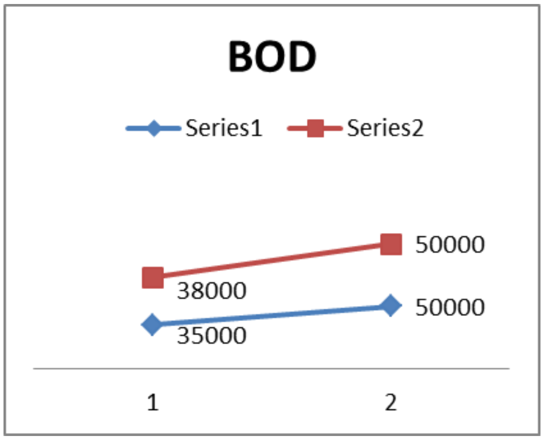


Fig. 4 Series 1: BOD of untreated effluent

Series 2: BOD of treated effluent

3.6.3 pH in effluent before treatment and after treatment

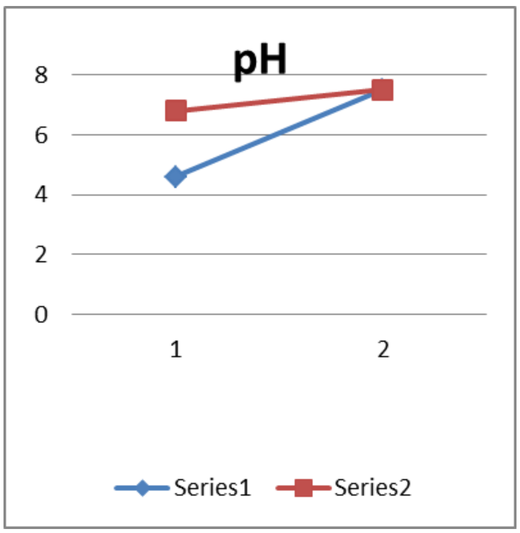


Fig. 5 Series 1: pH of untreated effluent

Series 2: pH of treated effluent

IV. Conclusion

One of the most important environmental problems faced by the world is management of wastes. Now-a-days emphasis is laid on waste minimization. Pollution prevention focuses on preventing the generation of wastes, while waste minimization refers to reducing the volume or toxicity of hazardous wastes by water recycling and reuse.

Here we conclude that the treatment are very important part of distillery spent wash, the major treatment as BOD concentration. We see that the BOD concentration is very high before treatment and it is reduces after treatment. If BOD values is high then the aquatic resion my not properly works

The low contents of DO which is toxic to plants, so itis not permissible for irrigation. Treated effluent of distillery plant which is well balanced of chemicalsif it is diluted with other fresh water, will be suitablefor irrigation purposes.

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