Impact of Distillery Effluent on Soil Quality

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ABSTRACT

The present work aims to determine the impact of distillery effluents in the soil samples and the quality of soil. The amount of pH and electrical conductivity present in the different soil samples are checked. The content of Nitrogen, Phosphorus, Potassium and available nutrients are determined. The cation exchange capacity of the soil and the rate of exchangeable bases are determined. With the above objective, a study was carried out at Soil Testing Laboratory, Tiruchirappalli, to know the impact of distillery effluent in the soil samples and the quality of soil.

Keyword: - Cation Exchange Capacity, Effluents, Electrical Conductivity, Nutrients, pH and Quality of Soil

1. INTRODUCTION

The term environment which means surrounding, is considered as a composite term for the conditions in which organisms live and thus consists of air, water, food and sunlight which are the basic needs of all living beings and plant life to carry on their life functions. The components of environment are lithosphere, hydrosphere and atmosphere [1].

Pollution is the unfavorable alteration of our environment, largely because of human activities. It can also be defined as a deviation from the natural composition of a part of the environment, resulting in adverse effects on life. Pollution is the accumulation of matter in the wrong place or anything that is released into the environment which degrades its quality. The different types of pollution are air, water and soil pollution. Soil pollution is referred to any adverse effect which is caused due to the alteration in physical, chemical and biological characteristics of soil [2].

Rapid urbanization, which the consequent increase in population and building construction, has resulted in the reduction of lands for the wastes to be disposed. Sources of soil pollution are industrial wastes, agricultural wastes, urban wastes, and radioactive pollutants, chemical and metallic pollutants. Disposal of industrial waste is a major problem responsible for soil pollution [3]. These industrial pollutants are mainly discharged from pulp and paper mills, chemical industries, oil refineries, sugar factories, tanneries, textiles, steel, distilleries, fertilizers, pesticides industries, coal and mining industries, metal processing industries, drugs, glass, cement, petroleum and engineering industries.

The disposal of these industrial wastes into the soil affect and alter the chemical and biological properties of soil. Many agricultural practices pollute the soil to a large extent. Today with the advancing agro-technology, huge quantities of fertilizers, pesticides, herbicides and soil conditioning agents are employed to increase the crop yield. Now a days agricultural practices rely heavily on artificial fertilizers, pesticides, herbicides which generally contain

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one or more of the plant nutrients such as nitrogen, phosphorous and potassium.

In addition to the fertilizers, pesticides and herbicides, soil conditioners and fumigants are also employed to the land system to increase and protect the soil fertility as well as to kill the hazardous insects. These chemical agents are reported to cause alterations in both agricultural and horticultural soil areas. They contain several toxic metals like lead, arsenic, mercury and cobalt, etc., which when applied to the land will accumulate on the soil permanently. Over population and increase consumption have totally changed the very complexion of domestic wastes into complex mixture of food remains, paper, plastic and many notorious chemicals [4].

Soil is one of the most significant ecological factor, which is derived from the transformation of surface rocks. Plants and animals depends on soil for their nutrients, water and mineral supply. The importance of soil may be realized from the statement of Sundar Lal Bahuguna – "The eternal truth that soil and water are the two significant capitals of mankind and the natural forest are the mothers of rivers and the factories of manufacturing soil". The soil provides homes and ideal environmental condition for living beings. Soil can be defined as the weathered layer of the earth's crust in which living organisms and their parts of decay are intermingled ^[5].

2. REVIEW OF LITERATURE

There are 285 distilleries in India producing 2.7 billion liters of alcohol and generating 40 billion liters of waste water annually. India has emerged during recent years on the largest sugarcane producer in the world. Most important of these is alcohol which bears immense significance as a basic chemical for rapidly advancing chemical industry and as a readily available source of energy ^[6]. Therefore there is a demand for alcohol will increase in the country and so also the number of distilleries. The proportion of waste water generally known as spent wash in nearly 15 times the total alcohol production. This massive quantity of effluent, if disposed untreated can cause considerable stress on the land courses leading to widespread damage to life ^[7].

Waste water from industries not only contain useful but also many harmful substances which convert the fertile land into a sterile one. The pre-treated effluent sources act as an additional potential source of fertilizer for agricultural purposes which other remain as an Environmental hazard. The spent was is the main type of effluent from distilleries. It is almost 100 times more concentrated than the domestic sewage. Considerable importance was not given to study the influence of distillery effluent in this regard (Haniffa & Sundarayadhanam, 1977) [8].

The physical, chemical and biological parameters of the spent wash from 12 distilleries have been already reported (Gurusamy et al., 1977 ^[9], Prasad et al, 1977 ^[10], Verma et al., 1979) ^[11]. Most of the wastes are applied to the land since soil is believed to have a capacity of receiving and decomposing wastes and pollutants of different kinds (Gopichandran, 2000) ^[12]. Wyatt (1988) ^[13] reported that the production of toxic waste effluents by the chemical industry is a major problem of disposal and steps should be taken by the industries for its disposal.

The first thing to do is to reduce the water outlet by establishing inner water circles where water is the circulating several times (Mullier et al., 1985) [14]. Swaminathan et al, (1989) suggested that recycling of distillery and chemical industries effluents is possible because of the fertilizer value of the effluents [15]. Agarwal and Panday (1994) reported that the spent wash has high capability of extracting out manganese from soil. The spent wash has thus been identified as an agent causing manganese deficiency in soil. When the rapid increase in the number of distilleries, there has been a substantial increase in liquid waste which is discharged either into land or nearby aquatic systems [16].

Dilip Kumar Panday and Prafulla Soni (1994) observed that the effluent was dark reddish brown in colour and had an odor similar to molasses. The effluent was found to be different in DO levels but contained high amounts of dissolved and suspended solids. Land is a receptor of many chemicals through the intentional and unintentional depositions such as landfills, spills, heaks, disposal (Singh and Nagar, 2001). Very good correlations were observed among the physico-chemical properties. These correlations are very helpful in knowing the association among the physic-chemical properties of effluents. The analysis of effluents release from different sources and characteristics of soil / ground water to the source of contamination has been carried out by das and Das, 2003. Distillery effluent is also one of the most complex, canamalised and cumbersome waste having very hight BOD & COD, which is highly toxic to environment with other organic and inorganic constituents (Singhal et al., 2003).

3. EXPERIMENTAL METHODS

3.1 Physico-Chemical Properties

Determination of pH

pH is a notation used for describing the acidity and alkalinity of a solution or soil. The potentiometric method was used to determine the pH.

Potentiometric Method

A glass electrode in contact with H^+ ions of the solution under test acquires an electrode potential, which depends on the concentration of H^+ ions. This is measured potentiometrically against the calomel electrode.

Soil: Water, 1:2 Method

20g of the soil was taken and transferred to 100 ml beaker, 40 ml of distilled water was added and stirred well and allowed to stand for 30 minutes with intermittent stirring. The pH meter was adjusted with a buffer solution and the electrode was immersed in the beaker which contained soil water suspension. The meter reading indicated the pH of the sample.

Determination of Electrical Conductivity (EC)

The method is based on the principle that conductivity of a solution of salt is nearly proportional to its concentration of salts. These electrical conductivity is measured in terms of the resistance offered to the flow of current using a conductivity bridge. Reagents required – Saturated solution of calcium sulphate and KCl solution (0.01N). 20g of the soil was taken in a 100 ml beaker, 40 ml of water was added, stirred and allowed it to stand for 30 minutes. Intermittent stirring was given. The electrode was immersed in the beaker containing soil water suspension. The meter reading directly indicated the conductance value of the soil samples.

3.2 Ion Exchange Analysis

Cation Exchange Capacity of Soils

The cation exchange capacity of a soil is the total negative charge of the soil measured under specific conditions. Its determination involves the saturation of all the charges by one cation. Conventionally, for soils with pH less than 7.0, NH_4^+ is the cation of choice and the determination is done at pH 7.0 by leaching the soil with ammonium acetate.

Reagents Required

- Ammonium acetate buffer solution (1.0 M)
- Ammonium chloride solution (1.0 M)
- Ethanol (95%) acid free
- Silver nitrate solution (0.1 M)
- Magnesium
- Mineral Oil
- Standard sulphuric acid (0.1 M)
- Boric acid solution (4%)
- Mixed indicator

Procedure

25g of the dry sample was taken in a 250 ml beaker and 75ml of ammonium acetate solution was added with constant stirring and allowed to settle overnight. It was filtered into a 250 ml conical flask. The sample was leached

with small portions of ammonium acetate solution. The leached soil was transferred to a kjeldahi flask immediately. 400 ml of water was added, followed by the addition of 2g of magnesium oxide, 5 drops of mineral oil, boric acid and indicator were added. It was distilled until 200ml has passed over. The unreacted boric acid was titrated against the standard sulphuric acid to the first tinge of red. A blank was carried without the soil.

Calculation

Cation exchange capacity of soil = 100 X C X (S-B)/W X (100-m)/100

Where

S = volume of sulphuric acid, sample, ml B = volume of sulphuric acid, blank, ml

C = normality of sulphuric acid W = weight of air dry sample, g M = air dry moisture content, %

Exchangeable Calcium and Magnesium Ions in Soil

The ammonium acetate extract is directly analysed for Calcium and Magnesium using an Atomic Absorption Spectrophotometry. The standards and extracts were prepared in the ammonium acetate solution. The alkaline earths were determined by complexometric titrations using EDTA. The Murexide was used as the indicator for calcium for Eriochrome black T for calcium and magnesium.

Reagents Required

- Hydrochloric acid
- Nitric acid
- Std. Ca solution (0.01 N)
- EDTA solution (0.01N)
- Buffer solution
- Sodium hydroxide solution
- Murexide indicator
- Eriochrome Black T indicator

Procedure

100 ml of ammonium acetate is pipetted out into a 400 ml beaker and it was evaporated to dryness. After cooling 5 ml of conc. HCl as added, wasing down the salts on the wall of the beaker, followed by 1 ml of conc HNO₃. It was covered immediately with a watch glass. When vigorous reaction had ceased, the solution was evaporated to dryness in the fume hood. After cooling, 1 ml of concentrated HCl and 20 ml of water were added and it was filtered into conical flask.

Calcium

20 ml nitrate was taken and 10 ml of NaOH buffer was added and then mixed well with murexide indicator and it was titrated against EDTA solution till the colour changes from red to purple.

Calcium and Magnesium

20 ml of the filtrate was pipeted out and 10 ml of ammonium hydroxide –ammonium chloride buffer and the indicator Eriochrome black T was added. It was titrated against the EDTA solution until the colour changes from red to permanent blue and also a blank was determined.

Calculations

For each calcium /100 g of soil= $(V_1-V_2)/V_3 *V_4 *C_1 *100/w *(100 -M)/100$

Where

 V_1 = volume of EDTA for sample

 V_2 = volume of EDTA FOR BLANK

 V_3 = volume of aliquot, ml

 V_4 = total volume of the ammonium acetate extract, ml

 C_1 = normality of EDTA

W = weight of air dry sample, g

M = air dry moisture content, %

For each Ca and Mg /100 g of soil = $(V_5-V_6)/V_7*V_8*C_2*100/W*(100-m)/100$

Where

 V_5 = volume of EDTA for sample

 V_6 = volume of EDTA for blank

 V_7 = volume of aliquot, ml

V₈ = total volume of original ammonium acetate extract, ml

 C_2 = normality of EDTA

W = weight of air dry sample

M = air dry moisture content, %

Exchangeable magnesium is calculated by the difference between the two values.

Sodium and Potassium

The ammonium acetate extract was analysed directly for sodium and potassium using a flame photometer. The standards were prepared in the ammonium acetate reagent and the values are read for standards and the sample against the reagent as blank.

3.3 Estimation of Available Nitrogen

Principle

For the determination of nitrogen supplying ability of the soil, it is mixed with excess of alkaline potassium permanganate and distilled organic matter present in the soil is oxidized by nascent oxygen liberated by potassium permanganate in the presence of sodium hydroxide and thus ammonia is released is distilled and is absorbed in boric acid and is titrated against acid using methyl red as indicator.

Reagents required

- 0.32 % KMNO₄
- 2.5 % NaOH
- 2% boric acid
- Double indicator
- · Sulphuric acid

Procedure

20 g of the soil was taken in distillation flask and 20 ml of distilled water was added followed by 100 ml of KMnO₄ and NaOH. The liberated ammonia was collected in a conical flask containing 20 ml of boric acid with double indicator. 30 ml of the distillate was collected and the colour changes to green with the absorption of ammonia for cooling. It was titrated against N/50 sulphuric acid. The end point being the appearance of blue colour.

Calculation

Amount of nitrogen = value *14

3.4 Estimation of Available Phosphorus

Phosphorus is extracted from the soil with 0.5 m sodium bicarbonate at nearly constant pH of 8.5. In acid soils containing aluminum and iron phosphates, phosphorus concentration in solution increases as the pH rises.

Reagents required

- Sodium bicarbonate
- Sulphuric acid
- Potassium di hydrogen phosphate

Procedure

5 g of the sample was taken and 50 ml of NaHCO₃ was added and shaken for an hour. It was filtered through Whatman filter paper and the filtrate was carefully collected. The 5 ml of filtrate, p-nitro phenol indicator was added followed by the addition of 5 N sulphuric acid. Then the solution is neutralized. Reagent B is prepared and made up to 1 liter. 5 ml of reagent B is added and then the filtrate is made up to 25 ml and the intensity of blue colour is measured using a red filter.

Preparation of Standard Graph

0.219 g of potassium dihydrogen phosphate was weighed and dissolved in 400 ml of water. Then 25 ml of 1 NH₂SO₄ was added and made up to 100 ml and as diluted to the required concentration as given in table.

Concentration required, N	Volume to be pipetted, ml	Volume to be made, ml	Meter reading	
0.1	0.5	25	20	
0.2	1.0	25	44	
0.3	1.5	25	70	
0.4	2	25	89	
0.5	2.5	25	114	
0.6	3	25	136	
0.7	3.5	25	162	
0.8	4	25	181	
0.9	4.5	25	217	
1.0	5	25	281	

Table 1: Standard Curve for Phosphorus

To the phosphorus solution, 5ml of Olsen's reagent was added and made up to 25ml of volume. The content was fed into the photoelectric colorimeter and the percent transmittance was noted. A graph was drawn between the percentage transmittances and concentration. The standard curve was used for finding out the concentration of phosphorus in the soil.

Phosphorus in soil (Kg/ac) = Solution in ppm * 50 (Olsen Method)

3.5 Potassium

The term available potassium incorporated both exchangeable and nonexchangeable forms of the nutrients present in soil. The readily exchangeable and water soluble potassium is determined in the neutral normal ammonium acetate extract of soil. The estimation of potassium in the extract was carried out with the help of flame photometer.

Principle

The principle involved in this estimation is that when the soil is treated with neutral ammonium acetate the ammonium ion replaces the potassium and other ions into the solution. The filtrate containing potassium is atomized on non-luminous flame. When the light of characteristic wavelength is given, atoms excite and at definite wavelength gives the characteristic lilac colour.

Reagents required

- Ammonium acetate
- · Standards solution of KCl

Preparation of Standard Curve

1.907 g of KCl is dissolved in 1 litre of water, then stock solution was prepared by diluting and various standards were prepared.

Concentration, N	Volume to be pippeted, ml	Volume to be made up, ml	Meter reading
10	10	100	28
20	20	100	45
30	30	100	57
40	40	100	67
50	50	100	75
60	60	100	82
70	70	100	87
80	80	100	92
90	90	100	97
100	100	100	100

Table 2: Standard Curve for Potassium

Procedure

5 g of sample was taken in a 100 ml conical flask and 25 ml of neutral ammonium acetate was added. The contents were shaken in a shaker and it was filtered. The flame photometer was set up and the instrument was made steady. The sample extract was fed and the meter reading was noted.

The standard graph was used for finding out the concentration of potassium in the soil sample.

Potassium in soil = solution in ppm X 5 Where 5 - dilution factor

3.6 Available Nutrients

Estimation of Available Zinc and Manganese

Material required

- Standard zinc solution
- Standard manganese solution
- Ammonium acetate

Procedure

5 g of soil was taken in a beaker and 50 ml of ammonium acetate was added and shaken for an hour. The solution was filtered and the concentration of the sample was directly analysed using the atomic absorption spectrophotometer.

Calculation

ppm in soil = ppm in solution X Volume of extract / Weight of soil taken

Estimation of Available Copper and Iron

Reagents required

- Standard copper sulphate solution
- Standard iron solution
- Normal Ammonium acetate

Procedure

5 g of soil was taken in a beaker and 50 mi of ammonium acetate was added and shaken for an hour. The solution was filtered and the reading was taken directly using atomic absorption spectrophotometer.

Table 3: Physico-Chemical Parameters of Experimental Soil

Parameter	No. of	Percentage of			
	Samples	Occurrence			
pН	1/1/80				
< 6.5	0	0			
6.5 - 8.5	0	0			
> 8.6	50	100			
Electrical Conductivity					
< 1	0	0			
1-3	16	32			
> 3	34	68			
Nitrogen	V				
< 113	44	88			
113 – 181	6	12			
> 181	0	0			
Phosphorus					
< 4.5	2	4			
4.5 - 9.0	6	12			
> 9.0	42	84			
Potassium					
< 47.5	0	0			
47.5 – 113	11	22			
> 113	39	78			

4. RESULTS AND DISCUSSION

4.1 pH

Depending on the nature, degree of watering and the extent of biological activities, the pH of the soils vary widely. A soil may be regarded as neutral, acidic, or alkaline if its pH value is equal to or greater or lesser than seven. Most plants prefer a near neutrality or slightly acidic conditions for their growth.

The pH of the samples vary from 8.6 - 10.4. The soils are mostly alkaline. Most soils are generally alkaline due to the presence of sufficient quantities of carbonate which is derived from the effluent water.

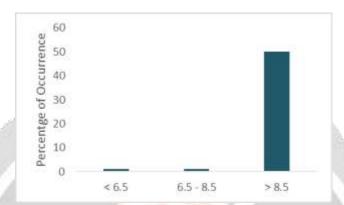


Chart 1: pH Status of the Experimental Soils

4.2 Electrical Conductivity

The conductivity of distilled water ranges between 1 to 5 mho but the presence of salts and contamination with waste water increases the conductivity of water. Most (68%) of the sample contained dissolved salts and about 32% of the sample has less amount of the salt.

The conductivity of the samples ranges from 7.6 - 13 mho cm⁻¹, reflecting the degree of pollutants. The large amounts of soluble salts, hinder plant growth, speed the corrosion of metal and produce an unpleasant taste in drinking water. In case of irrigation water, it is not suitable for plant growth. The soluble salts which are present in effluent or liquid water, can be removed by desaltation of good quality water.

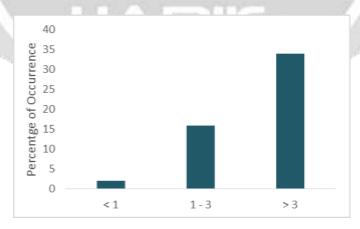


Chart 2: Electrical Conductivity of the Experimental Soils

4.3 Nitrogen

The nitrogen values ranges from 14.0 to 215.6 and 88 percent of the sample had the nitrogen content above 113. In case of nitrogen, fertilizers are not the only source of nitrogen in soil water, but also from decomposition of organic matter. In case of distillery effluent, large amount of organic matter is available and is decomposed and come to soil

solution. The most important factors that influence the amount of nitrate movement in soils are (1) the amount of nitrate dissolved in the soil, (2) the rate of its use by plants, (3) the rate of immobilization in to soil micro-organisms or newly synthesized soil organic matter, (4) the amount of water available for runoff and leaching through the soil, (5) soil permeability. Soil heavily dumped with effluent / sludge and soil naturally with fertility are potential source of nitrate contamination in soil solution 3 is quickly absorbed by a rapidly growing plant or by multiplying populations of soil micro-organisms, less is available to become leached. Nitrates are soluble ions but are not leached unless enough water exists to leach through the soil and the soil is permeable enough to allow leaching.

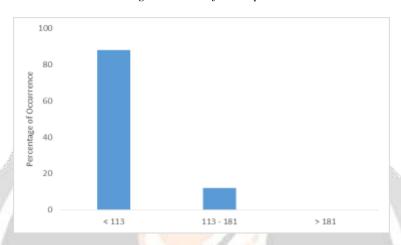


Chart 3: Nitrogen Content of the Experimental Soils

4.4 Phosphorus

The phosphorus content ranges from 1.25 -107.8 ppm in all the samples. About 84% of the sample had the values greater than 9 & 12 % had values between 4.5 – 9.0.Phosphorus is not a mobile nutrient in soils; it to easily form insoluble substances with many common cations. Because of its insoluble nature, phosphorus is often the limiting nutrient for algae and other plants growing in water. Only small amounts of phosphorus are leached from most mineral soils, but in organic soils low in iron oxides and aluminum phosphorus becomes relatively mobile and can be leached out as soluble organic phosphates. The major source of phosphorus contamination in soils is from direct dumping of industrial wastes [effluent water] and from eroded suspended solids from urban and rural wastes.

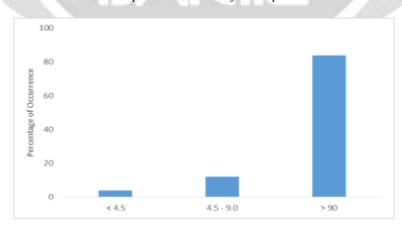


Chart 4: Phosphorous Content of the Experimental Soils

4.5 Pottassium

The potassium concentration of the samples measure ranged from 77.5 - 500 ppm. About 78% of the samples had the range above 113. The concentration of potassium is high in most of the soils, because the raw effluent contains more of potassium ions, due to the of equilibrium between primary minerals forms and exchanges calcium and water soluble potassium, the rate of availability of potassium is more.

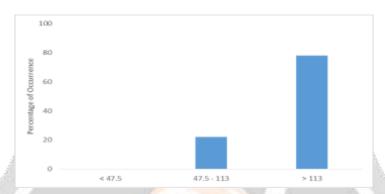


Chart 5: Potassium Content of the Experimental Soils

4.6 Cation Exchange Capacity

Ion exchange is the reversible process by which cations and anions are exchanged between soil and liquid phases and between solid phases that are in close contact with each other. Chemical and physical processes are intimately connected with ion exchange include weathering of mineral, nutrient absorption by plant, swelling and shrinkage of clay and leaching of electrolytes. Ion exchanges may be considered as the most important of all the processes occurring in the soil. The cation exchange capacity values ranges from 9.8 to 33.6.

4.7 Exchangeable Cations

The electric charge on the soil particles is neutralized by an equivalent amount of oppositely charged ions, the so called exchangeable ions, head to the surface by mainly coulomb forces. In addition to the coulomp forces, vanderwalss condon forces, increases the strength of bonding between certain ions. In our soils, the most exchangeable cations are Ca²⁺, Mg²⁺, H⁺, K⁺, Na⁺ and NH₄⁺ Calcium generally being the dominant ion, the relative abundance of the other ions varies greatly. In our soil, the sodium is exceptionally high. The capacity of soil to absorb and exchange cations and anions varies greatly with the content of clay and organic matter and the microbiological composition.

4.8 Micronutrients

These elements are essential to plant growth, but are utilized only in minute quantities, in contrast to the macronutrients, comprising of a proportionally large percentage of plant weight. The micronutrients arise from contaminant minerals mixed with the common primary minerals. The micronutrients like zinc, copper, iron and manganese are more soluble in acidic soil and hence more available in acidic soils, becoming less soluble as pH increases. In strong acid soils, manganese, zinc, copper may dissolve to from toxic concentrations that actually hinder plant growth. There are many interactions of micronutrients in the soil, making the maintenance of available nutrients a complex problem. Due to the alkaline nature of the experimental soils, the availability of micronutrients is normally less in all the soil samples.

5. SUMMARY

The soil pH provides various clues about the other soil properties. It greatly affects the solubility of minerals which are less concentration of soluble ammonia and manganese. The beans, barely and sugar beets do well in slightly

acidic to moderately basic soils because of high calcium demand. The soil pH can also influence plant growth through pH effect on activity of beneficial microorganisms. Unleashed soil or those high in calcium content may have pH values of 8.5 with increased exchangeable sodium ion. The major effect of a basic pH is to reduce the solubility of micronutrients especially those of iron, zinc, copper and manganese. The reduced growth of plant on soil is attributed to the pH value. The major effect of a basic pH is to reduce the solubility of micronutrients especially those of iron, zinc, copper and manganese.

Soil have low concentration in zinc, manganese and copper at high pH. The addition of phosphorus further decreases the availability of those metals at the root surface of just inside the root by precipitating them an insoluble phosphates. Most micronutrients problem is caused by high soil pH and neutralized by adding specific fertilizers. The deficiency of micronutrients caused by high soil pH can be compensated by adding specific fertilizers. These fertilizers should be water soluble complexes with the metal ions. The soil containing high concentration of sodium is reclaimed by the addition of gypsum followed by irrigation to leach the exchangeable sodium ion.

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