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PHYSICO-CHEMICAL ANALYSIS OF CONTAMINATED SOIL AND EFFLUENT COLLECTED FROM TANNERY INDUSTRIES IN DINDIGUL, INDIA

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ABSTRACT

Effluents from tannery industry is one of the major sources of coastal environmental pollution. The physico-chemical properties of effluents and soil in an industrial outlet area in Dindigul during January - May, 2017 have been analyzed. The parameters such as pH, Total Dissolved Solids, Total Alkalinity, Total Hardness, Calcium, Magnesium, Sodium, Chloride, Fluoride, Sulphate, and Phosphate and heavy metals like Copper, Iron, Magnesium, Chromium, Zinc etc., were analyzed using standard protocols. The effluent from the tannery industry was the major source of pollution which will affect the flora and fauna existing in the environment. Thus, there is need for further secondary treatment of tannery effluent before they are discharged in to the environment. The effluents are having the values higher than the permissible limit.

KEY WORDS : Pollution, Heavy metals, Soil analysis, Tannery, Effluent.

INTRODUCTION

Environmental pollution by industrial waste has increased tremendously with the rapid industrialization in the country. The quantities and characteristics of discharged effluent vary from industry to industry depending on the water consumption and chemicals utilized in the processing unit (Jothi and Santani, 2012). The dye and its related industries such as tannery are thus, potent hazards to the natural sources like soil, water, flora, fauna and human, population (Jaishree and Khan, 2014). A huge volume of mostly untreated tannery effluent is released into surface water and seep into the ground water and adjoining water bodies. Industrial effluent containing dyes, aniline, caustic soda, acids, heavy metals ions etc. and most of the heavy metals are essential for the growth of the organisms as micronutrient (Jaishree and Khan, 2014). The increasing concentration of heavy metals leads to bioaccumulation of metals in fauna and flora. As heavy metals are not biodegradable, they accumulate in primary organ in the body and lead to varies symptoms of diseases. Uncompleted or incompletely treated tannery effluent can be harmful to both aquatic and terrestrial life by adversely affecting on the natural ecosystem and long term health effects (Jaishree and Khan, 2014).

MATERIALS AND METHODS

Study area

The study area of Dindigul is located in the southern part of Tamil Nadu in India. Dindigul is one of the major industrial and commercial towns of Tamil Nadu and is the head quarters of Dindigul district. This area is known for its leather industries, some of them were established as early as 1939. Since then tanneries are multiplying and at present more than 80 are well established. Most of these are located in the centre of Dindigul town and along Madurai, Batlagundu and Ponamaravathi roads. Tannery waste is characterized by strong color (greenish). The growth of industrialization has been encroached

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even to small townships and villages along with all ills of pollution.

It is one of the tanning centers in Tamil Nadu. There are about 60 registered medium and small scale tanneries in clusters, which are located in and around Dindigul town. Due to lack of integration of environment considerations in the development of this region, the fast growth of the tanning industry in this belt has resulted in a drastic change in the environment. The tanneries which do not have effluent treatment including registered plants discharge the untreated effluent laden with salt and other pollutants like chromium, into tanks and low areas. Lagooning of tannery wastes, or spreading on land for evaporation, together with the concentration of ground water, pollutes the only source of drinking water and irrigation.

Collection of contaminated soil sample

The soil samples were collected from 0-30 cm deep locations immediate to the dumping site of effluent. The soil sample was collected in clean plastic bags washed with distilled water and dried

Physico-chemical analysis of contaminant soil

The soil samples were subjected to various physico-chemical analysis such as pH, Total Dissolved Solids, Total Alkalinity, Total Hardness, Calcium, Magnesium, Sodium, Chloride, Fluoride, Sulphate, and Phosphate using APHA (1995) method.

Collection of Tannery Effluent

The effluent was collected from outlet of tannery effluent located in Begambur near Dindigul in January, 2017. Samples were collected in wide mouthed plastic bottles. The plastic bottles were properly washed with detergent and distilled water prior to water collection and were carefully rinsed with sample effluent, filled up to the brim and tightly closed to ensure bubble-free sample storage.

Physico-chemical analysis of tannery effluent

Water quality analysis was carried out in the Tannery industry. The water quality parameters such as temperature, pH, acidity, alkalinity, hardness and macro & micro elements were analyzed.

Analysis of Heavy Metal by Atomic Absorption Spectroscopy (AAS)

Preparation of Standard Ion for AAS

The calibration plot method described in the British pharmacopoeia (2005) was adopted for the preparation of metal ion and Atomic Absorption Spectroscopy analysis.

Sample Preparation for AAS Analysis

The tannery effluent was filtered in a micro filter and it was used for analyzing the heavy metals by AAS.

The Analytical Technique

The analytical technique used to determine heavy metal level in all samples was thermo element Sys-813 Atomic Absorption Spectroscopy (International Equipment trading Ltd, USA). At each step of digestion processes, acid blanks (laboratory blank) were prepared in order to ensure that the sample and chemical used were not contaminated. They were analyzed by Atomic Absorption Spectrophotometer before the sample and their values were subtracted to ensure that equipment read only the exact values of heavy metal. Each set of digestion had its own acid blank and was corrected by using its blank.

Preparation of soil sample for heavy metal analysis

The soil sample was sieved through the plastic sieve to remove the large particles. Soil sample was placed overnight on oven at 150 ^{o}C till it dried. Sample was weighed 5gms in flask for the digestion. Then sample was digested by Hydrochloric acid and Nitric acid in 1:3 ratios. The sample was digested for 2 hours at 100 ^{o}C with reflex condenser. The soil was allowed to cool. It was filtered with Whatmann filter paper into 100 ml standard flask and it was used for heavy metal analysis.

RESULTS AND DISCUSSION

Physical parameters of effluent from tannery industry

The water quality parameters such as appearance, odour, turbidity, electrical conductivity and total dissolved solids were analyzed using tannery effluent.

Appearance and Odour

The tannery effluent sample showed greenish color with an objectionable odour. Odour of water is caused by chemical agents like hydrogen sulphide, free chlorine, ammonia, phenols, alcohols, esters, hydrocarbons and biological agents such as algae, fungi and other microorganisms (Sharma, 2000).

Turbidity

Turbidity of the tannery effluent was 37 NTU (Table 1). The colloidal and suspended impurities cause turbidity in the receiving effluent and reduce the light penetration into water and ultimately decrease the photosynthesis (Aisien *et al.*, 2010). In general it causes high turbulence and mixing of water leads to an increasing of the concentration of suspended particulate matter. Turbidity normally increases after heavy rain. The rain runs along the ground picking up small particles of dirt before reaching water source, hence increasing turbidity. Another study had pointed out that the surface water rich in turbidity suspends impurities of decaying organic matter, clay, microorganism like bacteria and small amount of minerals salts (Frada, 2001).

Electrical Conductivity

The electrical conductivity of tannery effluent was very high (Table 1). It is a measure of water's ability to conduct an electric current, and related to the amount of dissolved minerals in water, but it does not give an indication of which element is present; but high value of EC is a good indicator of the presence of contaminants such as sodium, potassium, chloride or sulphate (Nazir *et al.*, 2015).

Total Dissolved Solids (TDS)

The total dissolved solid of untreated effluent was high (Table 1). TDS in water originates from natural sources, sewage, urban and agriculture run off, municipal waste and chemical weathering of rocks (Hussain, 1989). Water containing extremely low concentration of TDS may also be unacceptable because of its flat and inadequate taste (WHO, 1994). TDS content in water is a measure for salinity. A high content of dissolved solid elements affects the density of water, influences osmoregulation of fresh water organisms and reduces solubility of gases and utility of water for drinking, irrigation and industrial purposes. Waters can be classified based on the concentration of TDS as, desirable for drinking and permissible for drinking (Wilcox, 1955).

Chemical examination of effluent from tannery industry

pH Value

The hydrogen ion concentration of the tannery effluent was alkaline (Table 2). pH is most important in determining the corrosive nature of water. Lower is the pH value; higher is the corrosive nature of water. pH is positively correlated with electrical conductance and total alkalinity (Gupta *et al.*, 2009). The reduced rate of photosynthetic activity, the assimilation of carbon dioxide and bicarbonates are ultimately responsible for increase in pH. Various factors bring about changes in the pH of water. Alkalinity was high in tannery effluent due to high pH (Table 2). The higher pH values observed suggests that carbon dioxide, carbonate-bicarbonate equilibrium is affected more due to change in physico-chemical condition (Karanth, 1987).

Table 1. Physical parameters of tannery effluent in Dindigul during 2017

Physical parameter of tannery effluent	Permissible Value in Normal water	Effluent sample
Colour	-	Greenish
Odour	-	Unobjectionable
Turbidity (NTU)	10	37
TDS (mg/l)	20	84
Electrical Conductivity (dS/m)	-	7803

Table 2. Chemical parameters of tannery effluent in Dindigul

Chemical parameters of tannery effluent	Permissible Value in Normal water	Effluent sample
pH	6.5	8.5
Total Alkalinity (mg/l)	-	45
Total Hardness (mg/l)	200	427
Calcium (mg/l)	-	456
Potassium (mg/l)	-	637
Nitrate (mg/l)	45	69

Total Hardness

Total hardness of the tannery effluent was 427 mg/l in Dindigul (Table 2). Hardness is defined as the concentration of multivalent metallic cations in a solution. The hardness of water varies from place to place. In general surface water is softer than groundwater. The hardness of water reflects the nature of geological formation with which it has been in contract (Garg *et al*., 2007).

Calcium (Ca)

Higher concentration of calcium was observed in the effluent of tannery as 456 mg/l (Table 2). Calcium is responsible for hardness of water and the addition of calcium in the fresh water system indicates that no removal has been taken place; it has precipitated in the lake water as the ionic strength has increased (Jayaprakash *et al.,* 2005). Calcium is an important element that is associated with different cations like carbonates, bicarbonates and fluorides. Ca^{2+} is directly related to hardness, higher Ca^{2+} contents increase hardness in water and make it unsuitable for domestic as well as agriculture purpose (Pirzada *et al.,* 2013).

Potassium (K)

Potassium concentration of tannery effluent was 637 mg/L (Table 2). Potassium is a dietary requirement for us, and we take up about 1-6 g per day at a requirement of 2-3.5 g per day. A study on potassium in the soil–plant system after land application of wastewaters was studied by Arienzoa *et al*. (2009). Conversely, an increase in concentration of potassium ion improved the settling properties of sludge (Murthy and Novak, 1998) and had a higher stimulating effect than inorganic salts and salt stress on microbial activity (Chandra *et al*., 2002).

Nitrate (NO_3) (Electrode Method)

The nitrate concentration in the tannery effluent was 69 mg/l (Table 2). Nitrate esters are capable of migrating over great distances and pose a threat (Rifler and Medina, 2006).

Dissolved Oxygen (DO)

The tannery effluent exhibits high values of dissolved oxygen at 27.5 m/l (Table 2). DO is one of the most important parameters. Its correlation with water body gives direct and indirect information e.g. bacterial activity, photosynthesis, availability of nutrients, stratification etc. (Vikal, 2009). Dissolved oxygen is very important for all physical and biological process going on in water. The analysis of dissolved oxygen is very important in water pollution and waste water analysis (Anoop and Renu, 2014).

Physico chemical analysis of contaminated soil

Physico chemical parameters of the soil collected near the outlet of the effluent from tannery industry was analyzed during January to May, 2017.

Table 3. Physico-chemical parameters of contaminated soil of Dindigul during 2017

Physico-chemical Parameters	Permissible Value in Normal Soil	Contaminated Soil
Ph	7	9.63
Available Nitrogen (ppm)	0.43	2.68
Phosphorus (ppm)	10.2	15.8
Potassium (ppm)	165	306
Electrical conductivity (ds/m)	-	0.37

Table 4. The difference between concentration of heavy metals in the tannery effluent and its soil

Heavy metals	Concentration of heavy metals in the effluent (mg/l)	Conc. of heavy metals in soil (mg/l)	Difference between the two medium
Zinc	0.0034	0.0048	-0.0014
Iron	0.0027	0.0035	-0.0008
Chromium	0.0049	0.0069	-0.002
Copper	0.0085	0.0063	0.0022
Magnesium	0.0065	0.0055	0.001
Lead	0.0035	0.0032	0.0003
Manganese	0.0043	0.0043	0

pH

In the present study P^H of the soil sample was very high and alkaline in nature (Table 3). In Sadli Reservoir soil, pH is usually increased when total alkalinity increases, but the balance of the added cations also has a marked effect on the soil pH, increasing the amount of sodium in an alkaline soil will tend to induce dissolution of calcium carbonate, which will increase the pH (Jayaprakash *et al*., 2005).

Available Nitrogen

In the present study, the value of nitrogen concentration in the soil sample was high (Table 3). Nitrogen existed in the soil system in many forms and changed very easily from one form to another. The route that nitrogen followed in and out of the soil system is collectively called the "nitrogen cycle". As the water drains through the soil, nitrate leaches out. Nitrogen is available to plants as either ammonium or nitrate. Animal manures and other organic wastes are the important sources of nitrogen for plant growth.

Phosphorous

In the present study, phosphorus concentration of soil sample exhibited as 15.8 ppm (Table 3). Phosphorus is an essential element for plant and animal growth, but too much of it can accelerate the natural aging of lakes and streams. Sediment Phosphorus, fixed to soil and organic material eroded during surface run off, provides a variable but long-term source of Phosphorus to algae in water bodies (Weil and Brady, 2017).

Potassium

In the present investigation, potassium concentration of the soil sample was 306 ppm. The main role of potassium is to provide the ionic environment for metabolic processes in the cytosol, and as such functions as a regulator of various processes including growth regulation. A deficiency of potassium ions can impair a plant's ability to maintain these processes. Potassium functions in other physiological processes and maintenance of cation: anion balance in the cytosol and vacuole (Hopkins, 2010).

Electrical Conductivity

In the present study electrical conductivity of soil sample was 0.37 ds/m (Table 3). Electrical conductivity (EC) is a measurement of the dissolved material in an aqueous solution, which relates to the ability of the material to conduct electrical current through it. Electrical conductivity, total dissolved solids and the level of Chloride, Sulphate, Iron, Ammonia, Nitrate, Phosphate, BOD, COD and DO were high in the effluent water, but Fluoride and Nitrite was within the standard limit of effluent water.

Heavy metal analysis of contaminated soil

Tannery effluent loaded Soil sample report showed the presence of various toxic heavy metals and sample contained zinc 0.0048 mg/l, iron 0.0035 mg/l, chromium 0.0069 mg/l, copper 0.0063 mg/l, magnesium 0.0055 mg/l, lead 0.0032 mg/l and manganese 0.0043 mg/l (Figure 1). In the present study, the high value of heavy metals was observed in Chromium followed by Copper and Magnesium.

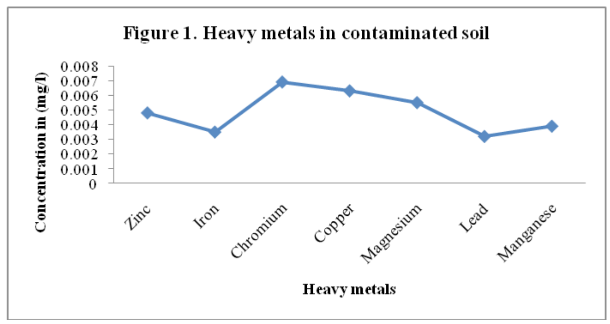

Fig. 1. Heavy metal analyses in contaminated soil of tannery effluent in Dindigul

The same result was obtained in bioremediation of heavy metals by employing resistant microbial isolates for agriculture soil (Kumar, 2006). The result was on a par with the study of Noorjahan *et al*. (2014) in the accumulation of heavy metals in the soil. Table 4 showed the vast difference when we compare the heavy metal concentration in tannery effluent and soil of the same spot. Zn, Fe and Cr had the capacity of holding high concentration of metals in soil than effluent whereas Mg, Pb and Cu were found higher in the effluent than soil (Table 4). Manganese concentration was the same in both the medium.

CONCLUSION

From the present investigation, the physicochemical parameters of the soil such as pH, available Nitrogen, Phosphorus, Potassium, Electrical conductivity and chemical parameters such as alkalinity, hardness, calcium, potassium and nitrate are above the permissible limit in soil and effluent.

The presence of heavy metal such as Chromium, Zinc, Iron are high in the effluent while Lead, Copper and Magnesium are high in the soil and Manganese was observed as the same. There is urgent need to follow adequate effluent treatment methods before their discharge to surface water for reducing their potential environmental hazards. Overall findings indicated that effluent discharge of tannery industry in Dindigul is highly polluted and remedial steps should be to taken for avoiding water and soil pollution which ultimately leads to biomagnifications in near future.

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