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STUDIES ON TREATMENT OF WASTEWATER FROM TANNERIES

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ABSTRACT

Due to the high conductivity of the global wastewaters from a tannery industries, wastewater reuse is only possible if reverse osmosis process is implemented in the wastewater treatment. The supernatant of a physical-chemical treatment is still very polluted, containing high COD values between 3000 mg/L to 4000 mg/L and conductivities of nearly 20 mS/cm. In this work, a combination of filtration, ultrafiltration and reverse osmosis is evaluated as treatment for the physical-chemically treated wastewater. Conventional treatment methods such as neutralization, clari-flocculation and biological processes are followed to clean the effluents before feeding to RO membrane modules. The characteristics of untreated composite effluents such as pH, COD, TSS, TDS and total chromium were in the range of 4.00-4.60, 680-3600 mg/L, 1698-7546 mg/L, 980-1480 mg/L, 4200-14500 mg/L, and 26.4-190 mg/L, respectively. Inorganic ions like Ca2+, Na+, Cl^- and SO_4^{-2} were found more in the wastewaters. Conventional treatments significantly removed the organic pollutants but failed to remove dissolved inorganic salts. Membrane technology removed the salts as well as remaining organic pollutants and the product water is reused in the process. The studied tanneries (5 numbers) have achieved 93-98%, 92-99% and 91-96% removal of TDS, sodium and chloride, respectively. Seventy to eighty five percentage of wastewater was recovered and recycled in the industrial processes.

INTRODUCTION

Tanning is one of the oldest industries in the world. During ancient times, tanning activities were organized to meet the local demands of leather footwear, drums and musical instruments. With the growth of population, the increasing requirement of leather and its products led to the establishment of large commercial tanneries. Two methods are adopted for tanning of raw hide/skin viz., vegetable tanning and chrome tanning. The production processes in a tannery can be split into four main categories: (1) Hide and skin storage and beam house operations, (2) tanyard operations, (3) post-tanning operations and (4) finishing operations.

Tanneries are typically characterized as pollution intensive industrial complexes which generate widely varying, high-strength wastewaters. Variability of tannery wastewaters are not only from the fill and draw type operation associated with tanning processes, but also from the different procedures used for hide preparation, tanning and finishing. These procedures are dictated by the kind of raw hides

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employed and the required characteristics of the finished product. Tanning industry also has one of the highest toxic intensity per unit of output. During tanning process at least about 300 kg chemicals are added per ton of hides. Tannery effluent is among one of the most hazardous pollutants of industry. Major problems are due to wastewater containing heavy metals, toxic chemicals, chloride, lime with high dissolved and suspended salts and other pollutants

LITERATURE REVIEW

Kanchinadham(2011) stated that Co-digestion studies were carried out for biogas generation using fleshings as the primary substrate and a mixture of primary and secondary sludge generated during the treatment of tannery wastewater as the co-substrate. Steapsin, a commercial grade lipase, was added to enhance the hydrolysis in anaerobic co-digestion. The lipase dosages used were ranging between 0.25 and 1.0g for a volatile solids input of 7.5g. The performance of the co-digestion was assessed from the volume of biogas generated. Experimental results revealed an optimum lipase dosage of about 0.75g. At this dosage, the biogas generation was observed to increase by about 15% compared to that in the control without adding lipase. Further, the digestion with lipase addition was observed faster since the digestion period was reduced about 30%. This means that the capacity of the digester could also be reduced about 30% leading to savings in its installation cost.

Durai (2011) investigated that Tannery wastewaters are highly complex and are characterized by high contents of organic, inorganic and nitrogenous compounds, chromium, sulfides, suspended solids and dissolved solids. Treatment of tannery wastewater is carried out by physical or chemical or biological or combination of these methods. This study reviews various biological treatment methods applied for tannery wastewater. Characteristics of wastewaters from different tanneries and various methods for treating these tannery wastes are discussed. It was noted that the Chemical Oxygen Demand (COD) removal efficiencies and process capacities were affected by the variations in organic loading rates, presence of chromium and sulfides. The review shows that all aerobic processes have a similar level of COD removal, but the highest COD removal efficiency at a high organic loading rate was observed in anaerobic reactors. Up flow Anaerobic Sludge Blanket Reactor (UASB) exhibited better performance for treating high strength tannery wastewater effectively, compared with conventional reactors. Both aerobic and anaerobic processes are employed for the treatment of tannery wastewater. From the review it can be concluded that physical/chemical processes combined with biological process is the better option for the treatment of tannery wastewater.

Islam (2011) studied that the physico-chemical parameters of tannery effluents as well as the treatment efficiency of alum, ferric chloride and lime, addressed as different treatments. Pollutant removal efficiency was measured in terms of reduction in value of total solid (TS), suspended solid (SS), total dissolved solid (TDS), color, pH, C^{-1}, Alkalinity, biochemical oxygen demand (BOD5), chemical oxygen demand (COD), Cr6+ and salinity.While analyzing the physico-chemical parameters of the tannery effluents, before treating with coagulants, the odor of the effluents was found to be invariably objectionable. After treatment of the tannery effluents, the lowest value for color (246.67 in Hazen unit) was found in the treatment T5, pH value 7.13 was found in treatment T7 followed by 7.23 in T2 and T6, the lowest TS (3833.33 mg/L) was recorded in the treatment T5 and SS observed as 0 mg/L in case of both T5 and T1 treatments. Cr6+ concentration was reduced considerably in treatment T5 (0.03 mg/L) and T7 (0.07 mg/L). Reduction in values of TDS, alkalinity, salinity, C^{-1}, BOD_5 and COD in treated effluents was also notable. The study recommended the combination of alum and ferric chloride (T5) as well as alum (T1) for the effective primary treatment of tannery effluents.

Belay (2010) focused on the challenges/impacts of tannery effluent and evaluates the alternative treatment options used to treat, recover or recycle chromium from the waste water. The paper was done entirely on secondary data by consulting literature sources including scientific journals, chapters of books, conference report papers and websites. The results of this review paper indicated that chromium is highly toxic and carcinogenic to human beings, animals, plants and the general environment (soil and water sediment). It is found out that chromium is the primary threat when ever tanning industry comes in to practice. Though many treatment options were evaluated to prevent its consequence on the environment, neither of them could achieve to treat or recover the chromium to 100%. Treatment options are either; inefficient, complicated, energy demanding, costly or applicable to a certain parts of the world due to technology or skilled man power demand. Therefore, to tackle this serious challenge stringent environmental regulation with law enforcement has to be exercised to use better treatment system which is widely applicable. Polluters must also know the environmental cost of their industry and treated according to polluter pay or precautionary principles. Moreover, the general public has to be aware of it and all concerned organizations and governments has to work hand in hand to reach zero discharge level or at least to attain the EPA chrome discharge limits.

Ranganathan (2011) investigated that tanneries reusing wastewater by combination of conventional and advanced Reverse Osmosis (RO) treatment technologies were assessed for technical and economic viabilities. Conventional treatment methods such as neutralization, clari-flocculation and biological processes are followed to clean the effluents before feeding to RO membrane modules. The characteristics of untreated composite effluents such as pH, biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), total dissolved solids (TDS), and total chromium were in the range of 4.00-4.60, 680-3600 mg/L, 1698-7546 mg/L, 980-1480 mg/L, 4200-14500 mg/L and 26.4-190 mg/L, respectively. Inorganic ions like Ca2+, Na+, C^{1-} and SO4^{2-} were found more in the wastewaters. Conventional treatments significantly removed the organic pollutants, however failed to remove dissolved inorganic salts. Membrane technology removed the salts as well as remaining organic pollutants and the product water is reused in the process. The studied tanneries (5 numbers) have achieved 93-98%, 92-99% and 91-96% removal of TDS, sodium and chloride, respectively. Seventy to eighty five percentage of wastewater was recovered and recycled in the industrial processes. The rejects are subject to either solar evaporation system or Multiple Effect Evaporation (MEE) technology. The resulting salts are collected in polythene bags and disposed into scientifically managed secured land fill (SLF) site.

MATERIALS AND METHODS

The waste water samples collected from tannery industry. The waste water was analyzed in the laboratory for the parameters such as Color, Chemical Oxygen Demand (COD), pH, TDS, TS, Chromium analysis, Chloride estimation etc. The process flow diagram for effluent treatment plant is shown in Fig 1.

Experiments were conducted in a 250 mL Erlenmeyer flask. The effect of pH on degradation of tannery wastewater was studied. 100 mL of wastewater obtained from tannery industry was taken in the batch reactor and seed sludge 2 % (v/v) was added

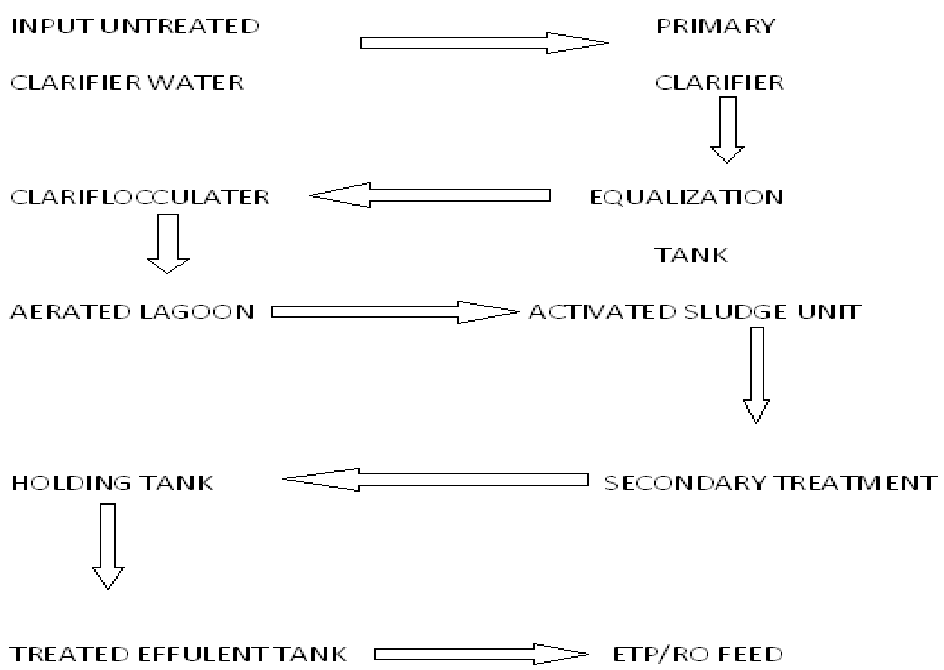

Fig.1 Effulent treatment process flow

to it. The pH of the wastewater was adjusted to 5, 6, 7 and 8 by adding acid or base as required. Sulfuric acid and sodium hydroxide were used as acid and base respectively. The COD of the wastewater in each batch reactor were measured at regular time intervals. The effect of temperature was studied in the range of 20-35°C. The effect of inoculums concentration was studied by adjusting the concentration by 1% to 4%. The effect of agitation speed was carried out in the range of 125 – 200 rpm. The initial concentration of tannery wastewater varied to give approximately 1560, 3220, 4680 and 6240 mg COD/L. 150 mL of each sample is taken in separate batch reactor and 2% (v/v) seed sludge was added to each flask. The reduction in COD was recorded at regular time intervals and reported in terms of % COD reduction.

RESULTS

As the sample was taken from primary clarifier which was untreated waste water, so it contains many hazardous organic compounds like chromium. Waste water treatment was given by the use of lime, alum and carbon and also other parameter like COD, TS, TDS, TSS, Chloride, sulphate were analyzed. The COD of untreated sample was 5208 mg/L. Initial chrome was 38.47 mg/L. On giving treatment with lime, the pH of sample increases. Generally, for lime the pH was adjusted between 6.5 – 9.5 to achieve maximum metal hydroxide precipitate. Then, on adding alum the maximum settlement was seen at pH 8.5 to 8.7 and reduction in chromium content was also observed. Now, as the carbon has adsorption property, so on adding carbon it adsorbs the chromium and finally we get the removal of chromium content i.e., 0.72 mg/L.

DISCUSSION

From Fig 2. After treatment of waste water, reduction of COD found, as Fig. 2 shows that on day one COD was 8723 mg/L and after treatment COD was found to be 2760 mg/L, day two COD was 6987 mg/L and after treatment it was 3212mg/L, day three COD was 7154 mg/L and after treatment COD

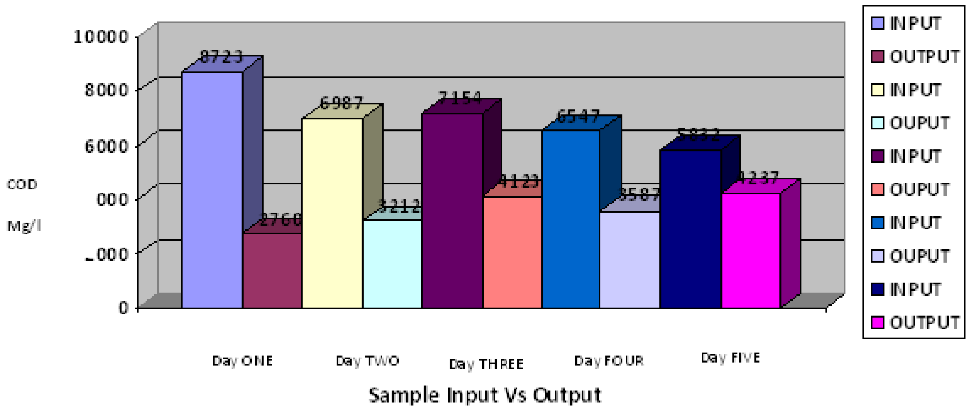

Fig. 2 Chemical oxygen demand

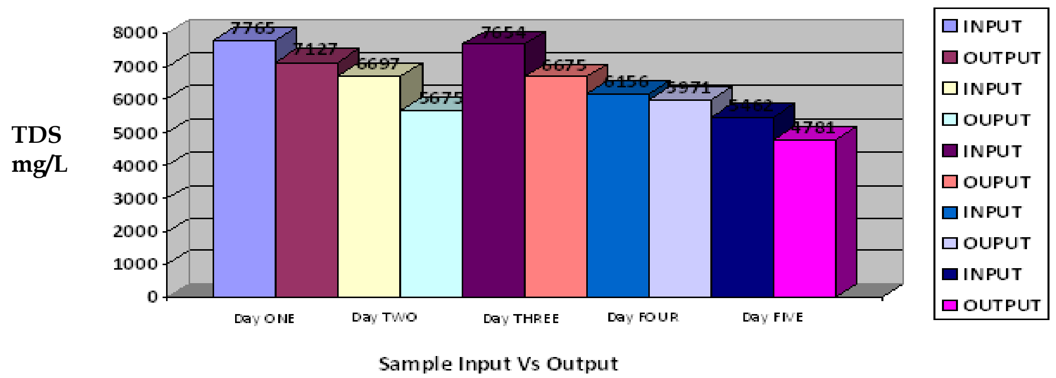

Fig. 4.Total dissolved solid

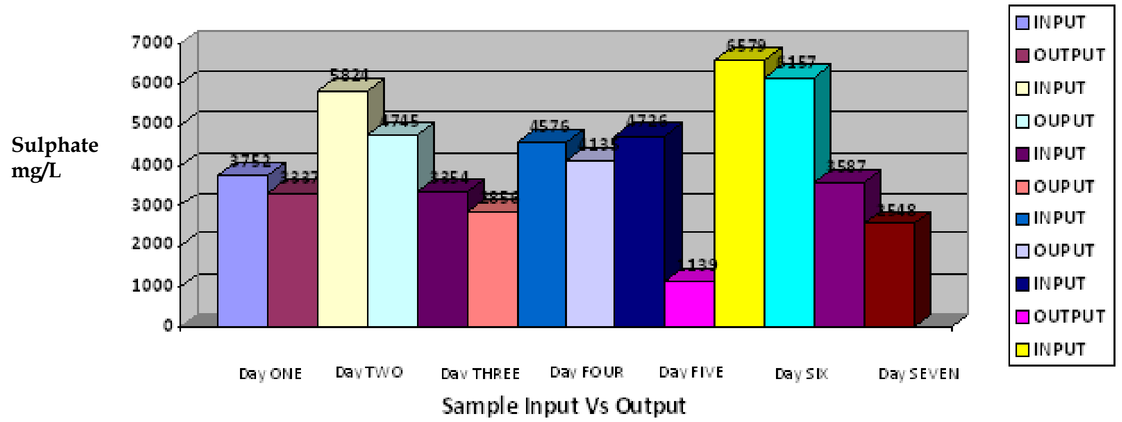

Fig. 5 Sulphate values during the treatment

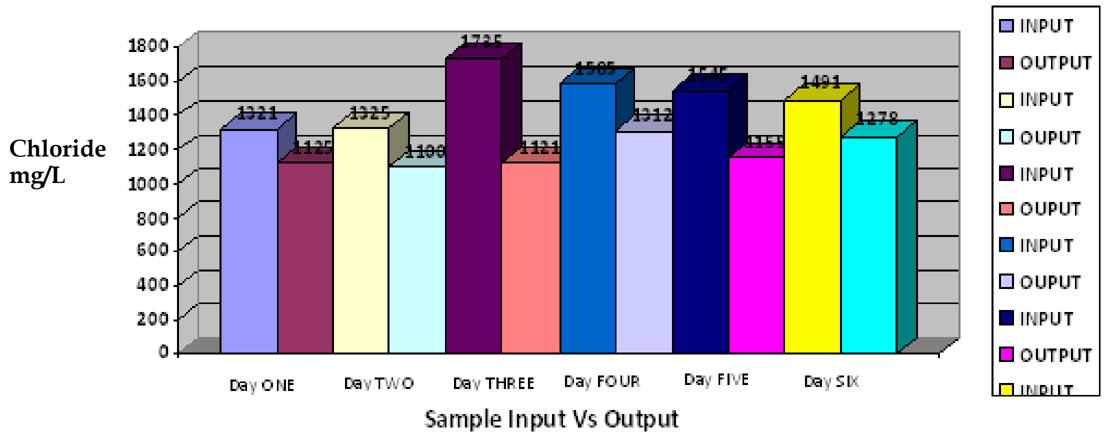

Fig 6 Chloride during the treatment

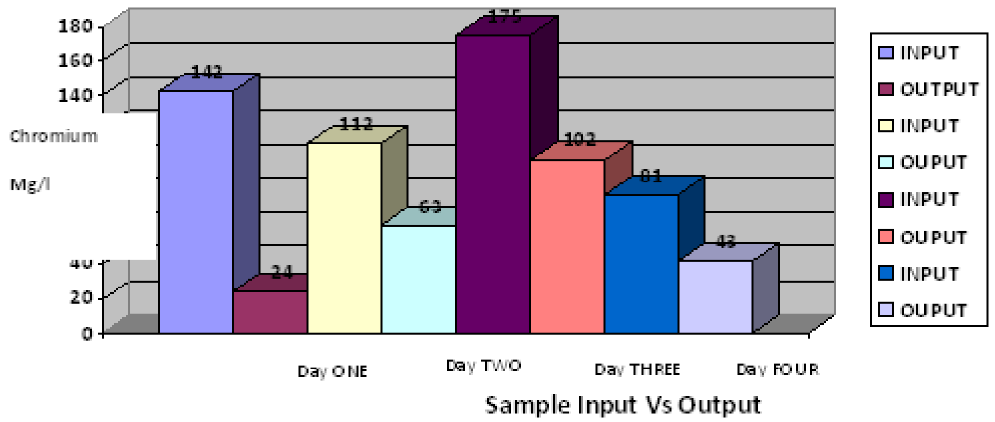

Fig. 7 Chromium during the treatment

was found to be 4143 mg/L, day four COD was 6547 mg/L and after treatment COD was found to be 3587 mg/L and day five COD was 5832 mg/L and after treatment COD it was 4237 mg/L, organic matter in industrial waste water that contains compounds that are toxic to biological life are reduced.

From Fig. 3 after treatment of waste water, reduction of total solid found, as graph shows that on day one TS was 8542 mg/L and after treatment it was 7785 mg/L, day two TS was 7654 mg/L and after

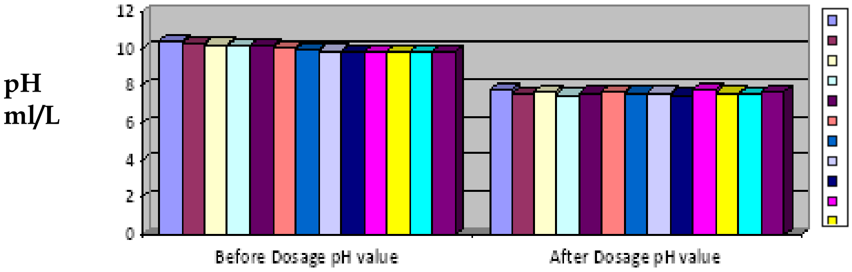

Fig. 8 pH observation

treatment TS was found to be 5762 mg/L, day Three TS was 6543 mg/L and after treatment it was found to be 5463 mg/L, day four TS was 7654 mg/L and after treatment it was found to be 5438 mg/L and day five TS was 6773 mg/L and after treatment TS was found to be 5984 mg/L, Organic and inorganic solids, suspended solids in industrial waste water are reduced after filtration.

As Fig. 4. shows that after treatment of waste water TDS were reduced, as graph shows on day one TDS were 7765 mg/L and after treatment TDS were found to be 7127 mg/L, day two TDS were 6697 mg/L and after treatment they were 5675 mg/L, day three TDS were 7654 mg/L and after treatment they were 6675 mg/L, day four TDS were 6156 mg/L and after treatment TDS were found 5971 mg/L and day five TDS were 5462 mg/L and after treatment they were 4781 mg/L, the total dissolved solids concentration is the sum of the cat ions (positively charged) and anions (negatively charged) ions in the water is reduced.

As Fig 5. shows on day one Sulphates were 3752 mg/L and after treatment Sulphates were found to be 3337 mg/L, day two Sulphates were 5824 mg/L and after treatment Sulphates were found to be 4745 mg/L, day three Sulphates were 3354 mg/L and after treatment Sulphates were found to be 2854 mg/L, day four Sulphates were 4576 mg/L and after treatment Sulphates were found to be 4135 mg/L and day five Sulphates were 4726 mg/L and after treatment Sulphates were 1139 mg/L and so on , Sulphate analysis shows that sulphate reduced after treatment of wastewater in industry.

As Fig 6. shows that Chlorides are highly soluble in water, which reduce micro filters/reverse osmosis. As graph shows on that day one Chlorides were 1321 mg/L and after treatment Chlorides were found to be 1125 mg/L, day two Chlorides were 1325 mg/L and after treatment Chlorides were found to be 1100 mg/L, day three Chlorides were 1735 mg/L and after treatment Chlorides were found 1121 mg/L, day four Chlorides were 1585 mg/L and after treatment Chlorides were found to be 1312 mg/L and day five Chlorides were 1545 mg/L and after treatment Chlorides were found 1155 mg/L and so on. After treatment a substantial reduction was found in Chloride percentage.

Fig. 7. shows that Chromium reduction is achieved by reaction of Cr+6 with a reducing agent. The most commonly used reducing agents are sulfur dioxide gas and sodium metabisulfite (dry granular power). Alternative reducing agents include: sodium hydrosulfite, ferrous sulfate and iron or steel scrap. As the figure shows on day One Chromium was 142 mg/L and after treatment it was to be 42 mg/L, day two Chromium was 112 mg/L and after treatment it was 63 mg/L, on day Three Chromium was 175 mg/L and after treatment it was 102 mg/L, and on day four Chromium was 81 mg/L and after treatment it was 43 mg/L. Graph shows chromium reduction.

As Fig. 8 shows that basic value of waste water decreased after HCL dosing, it reaches near neutral or pure water pH range after final treatment.

REFERENCES

Maiti, S.K. 2001. *Handbook of Methods in Environmental Studies,* Volume -1 *Water and Waste Water Analysis*. ABD Publishers Jaipur India.

Nesaratnam, S. 1998. *Effluent Treatment*. Leatherhead, Surrey: Pira International.

Nazaroff William, W. and Cohenb Lisa, Alvarez, 2004. *Environmental Engineering Science*. John Willy & sons (Asia) Pvt. Ltd., Singapore.

Pittner, G.A. 1993. The Economics of Desalination Processes. Chapter 3 in *Reverse Osmosis: Membrane Technology, Water Chemistry, and Industrial Applications*. Edited by Z. Amjad. New York: Van Nostrand Reinhold.

Tchobanoglous, G., Burton, F. and Metcalf & Eddy, 1995. *Wastewater Engineering: Treatment, Disposal, Reuse.* 3rd Edition, Tata McGraw-Hill, New Delhi, India.