PHYSICO-CHEMICAL ANALYSIS OF EFFLUENTS FROM PHARMACEUTICAL INDUSTRY AND ITS EFFICIENCY STUDY

R.V.Kavitha[1], V Krishna Murthy[1] Roshan Makam, [1] Asith K A[1]
[1]Department of Biotechnology /CORI, PESIT, BSK III Stage, Bangalore-85, India

Abstract: There is an increasing trend to require more efficient use of water resources, both in urban & rural areas .The aim of the present research work was to determine the behavior of various parameters of the pharmaceutical wastewater. The company produces bulk drugs, antibiotics, pain killers, food additives, personal care products and others. It is important for the industry to develop its own wastewater treatment system before discharging the effluent in order to meet the Karnataka State Pollution control Board (KSPCB) standards. Reduction of pollutants in the wastewater down to permissible concentrations is necessary for the protection of ground water and the environment. In order to design an appropriate treatment system the characteristic of the wastewater generated need to be found out with reference to the following parameters; temperature, pH, total suspended solids (TSS), total dissolved solids (TDS), Biochemical oxygen demand (BOD), Chemical oxygen demand (COD), oil & grease, chlorides & sulphates An intensive analytical programme was followed for 4 months for monitoring pharmaceutical wastewater. The characteristics of the waste water for the inlet to outlet for the septic tanks variations were TSS ranged between 4300-94 mg/L, TDS ranging between 2846-1308 mg/L, COD ranging between7280-9.9mg/L, BOD ranging between 4132-6.6 mg/L, chlorides ranging between 1000-300 mg/L, sulphates between 500-300 mg/l and pH ranging between 7.43-7.14 mg/L. Evaluation of data presented revealed that the order of reduction efficiency was COD < TDS < BOD < TSS. Additionally, the problems associated with the operation and maintenance of wastewater treatment plants is discussed.

Key words: Antibiotics; Efficiency; Permissible concentrations; Pharmaceutical wastewater

Introduction:

In view of high cost of conventional wastewater treatment systems there is an increasing need to develop low cost methods of treating wastewater particularly that of municipal and industrial origin. Rapid industrialization has resulted in the rise of pollution. To counter the above shortcoming and to preserve the high quality of the environment new concept so called "*Cleaner Production*" for waste minimization is being introduced, technology designed to prevent waste emission at the source of generation itself (Uwadiae *et al* 2011). Developing low cost technology for wastewater treatment offers an alternative and has been found to be most effective for treatment of domestic and industrial wastewater, particularly for those situated in the tropical and subtropical regions (NgMiranda *et al*., 1989; Puskas *et al*., 1991; El-Gohary *et al*., 1995; Rosen *et al*., 1998; Larsen *et al*., 2004). Technologically because of the simplicity of waste stabilization ponds even affluent nations, which can afford the luxury of expensive wastewater treatment, are planning to use more and more low cost treatment technologies (Khan and Ahmad, 1992; Junico and Shelef, 1994).

Environmental degradation is an escalating problem owing to the continual expansion of industrial production and high-levels of consumption. A renewed dedication to a proven strategy to resolve this problem is needed. Cleaner Production is one such strategy, which can address this problem. It is a preventive environmental management strategy, which promotes eliminating waste before it is created to systematically reduce overall pollution generation, and improve efficiencies of resources use. (Hashmi Imran 2005).

Wastewater pollution is the main issue of this sector. In pharmaceutical industries wastewater is mainly generated through the washing activities of the equipment. Though the wastewater discharged is small in volume, is highly polluted because of presence of substantial amounts of organic pollutants (Overcash, 1986). Solid waste usually comprises of expired or rejected medicines, spent solvents, packaging material and damaged bottles. Level of wastewater pollution varies from industry to industry depending on the type of process and the size of the industry (Garcia *et al*., 1995).

Hence Effluent Treatment Plants or ETPs are used by leading companies in the pharmaceutical and chemical industry to purify water and remove any toxic and noneffluent-treatment-plant toxic materials or chemicals from it. These plants are used by all companies for environment protection.

The ETP plants are used widely in pharmaceutical industry to remove the effluents from the bulk drugs. During the manufacturing process of drugs, varied effluents and contaminants are produced. The effluent treatment plants are used in the removal of high amount of organics, debris, dirt, grit, pollution, toxic, non toxic materials, polymers etc. from drugs and other medicated stuff. The ETP plants use evaporation and drying methods, and other auxiliary techniques such as centrifuging, filtration, incineration for chemical processing and effluent treatment. The effluent water treatment plants are installed to reduce the possibility of pollution; biodegradable organics if left unsolved, the levels of contamination in the process of purification could damage bacterial treatment beds and lead to pollution of controlled waters.

The aim of the present research work was to determine the behavior of various parameters of the pharmaceutical wastewater. Characterization of wastewater was evaluated in terms of temperature, pH, total suspended solids (TSS), total dissolved solids (TDS), Biochemical oxygen demand (BOD), Chemical oxygen demand (COD), oil & grease, chlorides & sulphates for the influent & effluent from the selected plants. The performance of the effluent treatment plant was also evaluated & the quality of the reclaimed wastewater was compared with Karnataka State Pollution control Board (KSPCB) standards to determine its suitability for reuse.

MATERIALS AND METHODS

The source for the collection of wastewater samples throughout the present studies was the Pharmaceutical industry. The study was conducted in a Pharmaceutical industry located in Bangalore, Karnataka. The methodology involved the collection of samples at the different units of the treatment plant.

The effluent treatment plant consists of primary, secondary & tertiary treatments which comprises of collection tank (CT), screening chambers, equalization tank, neutralization tank primary clarifier (PC), anaerobic lagoon, Extended anaerobic lagoon, aerobic lagoon, extended aerobic lagoon, aeration tank-1(AT-1), aeration tank (AT-2), settling tank, reverse osmosis (RO), and sludge drying beds (SDB).

Present research study was conducted for a period of 4 months, the wastewater samples were collected using sterile one liter plastic containers. Samples were collected in pre-sterilized bottles from equalization tank, neutralization tank primary clarifier (PC), anaerobic lagoon, Extended anaerobic lagoon , aerobic lagoon, extended aerobic lagoon, aeration tank-1(AT), aeration tank (AT-2), settling tank and reverse osmosis (RO), for physicochemical analysis (pH, Temperature, COD, BOD, chlorides, sulphates, TSS, TDS, DO and hardness). All samples were transported to the laboratory and analyzed within 30 min. All parameters were analyzed in accordance with standard methods of KSPCB.

RESULTS AND DISCUSSION:

Data taken during 4 months of this study are presented and discussed. The Concentration of these pollutants should not be allowed to go beyond a certain range, and extra care should be taken to avoid shock load. In case of shock load and abnormal introduction of BOD5, COD, oil and grease etc. Equalization process is recommended before chemical treatment.

Analysis of sample

The samples were analyzed for the following parameters:

pH: pH of the individual sample was measured immediately after its collection by a pH meter. The results are shown in Table 1 and 2 and Figure 1. The pH of wastewater samples is generally as low as 7.29 and was as high as 7.81 before the treatment. Hashmi Imran (2005) reported that the pH of wastewater samples is generally towards acidic side. It was as low as 5.0 and was as high as 7.2 before entering the septic tank. Extremes of pH of wastewater are generally not acceptable as extremes of pH cause problems to survival of aquatic life. It also interferes with the optimum operation of wastewater treatment facilities. Water with high or low pH is not suitable for irrigation. At low pH most of the metals become soluble and become available and therefore could be hazardous in the environment. At high pH most of the metals become insoluble and accumulate in the sludge and sediments. The findings of the present study are in agreement with the KSPCB standards (Table 3).

Total suspended solids (TSS): Suspended solid do not mean that they are floating matters and remain on top of water layer. They are under suspension and remain in water sample. Total suspended solids play an important role in water and waster water treatment. Their presence in water sample cause depletion of oxygen level. The values for TSS are shown in Table 1 and 2. The minimum and maximum values ranged between 100-4300(before entering the tanks) and 100-2500 mg/L (after leaving the tanks). The TSS value in our study was 94 mg/l which were in accordance with the KSPCB standards (Table 3). TSS is an important parameter for designing wastewater treatment plant and the length of time for which wastewater should be retained for primary treatment.

Total dissolved solids (TDS): The total solid concentration in waste effluent represents the colloidal form and dissolved species. The probable reason for the fluctuation of value of total solid and subsequent the value of dissolved solids due to content collision of these colloidal particles. The rate of collision of aggregated process is also influenced by PH of these effluents.
The values for these parameters are shown in Table 1 and 2, Figure 4. The minimum and maximum values ranged between 1920-2846(before entering the tanks) and 1308-2846 mg/L (after leaving the tanks). The averaged values ranged between 2272-2132 mg/L for both the influent & the effluent are well within the maximum permissible limits of 3500 mg/L according to KSPCB standards (Table 3).

Chemical oxygen demand (COD): The chemical oxygen demand test (COD) determines, the oxygen required for chemical oxidation of organic matter with the help of strong chemical oxidant. The COD is a test which is used to measure pollution of domestic and industrial waste. The waste is measure in terms of equality of oxygen required for oxidation of organic matter to produce CO_2 and water. It is a fact that all organic compounds with a few exceptions can be oxidizing agents under the acidic condition. COD test is useful in pinpointing toxic condition and presence of biological resistant substances.

For COD determination samples were preserved using H_2SO_4 and processed for COD determination after the entire sampling operation was complete. The results are shown in Table 1 and 2, Figure 2. As compared to BOD, COD was very high which is normal for such pharmaceutical industries. The minimum and maximum values ranged between 136-7280(before entering the tanks) and 99-7212 mg/L (after leaving the tanks). The averaged values ranged between 3186-1953 mg/L for both the influent & the effluent. Our study showed that the COD after treatment of wastewater was 99 mg/L which was well within the maximum permissible limits of 100 mg/L according to KSPCB standards (Table 3).

Biochemical oxygen demand (BOD): For BOD5 samples were immediately processed after Collection for the determination of initial oxygen and incubated at 20 °C for 5 days for the determination of BOD5. The results are shown in Table 1 and 2, Figure 3. The minimum and maximum values ranged between27-4132 (before entering the tanks) and 6.6-4096 mg/L (after leaving the tanks). The averaged values ranged between 1744-1369 mg/L for both the influent & the effluent. The present study reveled that the BOD after treatment was found to be 6.6 mg/L which was well within the maximum permissible limits of 10 mg/L according to KSPCB standards (Table 3).

Chlorides: Chlorides are generally present in natural water. The presence of chloride in the natural water can be attributed to dissolution of salts deposits discharged of effluent from chemical industries, oil well operations, sewage discharge of effluent from chemical industries, etc.In the present study chloride of untreated effluent was 1000mg/l and treated effluent was 300 mg/L which was within the permissible limits of 350 mg/ L according to the KSPCB standards (Table 3).

Sulphates: Sulphate in one of the major cation occurring in natural water. Sulphate being a stable, highly oxidized, soluble form of sulphur and which is generally present in natural surface and ground waters. Sulphate itself has never been a limiting factor in aquatic systems. The normal levels of sulphate are more than adequate to meet plants need. When water is over loaded with organic waste to point that oxygen is removed then sulphate as an electron acceptor is often used for break down of organic matter to produce H_2S and produce rotton egg smell (Welch, 1980).In the present study the values of sulphate for untreated effluent was 500 mg/l and that of treated effluent was 300 mg/l which was within the permissible limits of 1000 mg/ L according to the KSPCB standards (Table 3).

Table 1.Physico-Chemical Parameters of wastewater entering the tanks.

Tank /parameter	pH	TDS mg/l	TSS mg/l	BOD mg/l	COD mg/l	Chlorides mg/l	Sulphates mg/l
Neutralization tank	7.43	2846	----	4132	7280	----	----
Equalization tank	7.35	2846	----	4096	7212	----	----
Primary clarifier	7.23	----	4300	4043	7113	1000	500
Anaerobic lagoon	7.81	2844	----	4002	6903	----	----
Ext.anaerobic lagoon	7.41	2724	----	1609	3451	----	----

Aerobic lagoon	7.41	2652	----	753	1602	----	----
Ext.Aerobic lagoon	7.31	2583	----	316	665	----	----
Aeration tank	7.3	2411	----	125	344	----	----
Ext. aeration tank	7.3	2140	----	57	211	----	----
Settling tank	7.29	2032	----	27	138	----	----
Reverse osmosis plant	7.29	1920	100	27	136	300	300

Table 2.Physico-Chemical Parameters of wastewater leaving the tanks.

Tank/ parameter	pH	TDS mg/l	TSS mg/l	BOD mg/l	COD mg/l	Chlorides mg/l	Sulphates mg/l
Neutralization tank	7.35	2846	----	4132	7212	----	----
Equalization tank	7.23	2846	----	4096	7117	----	----
Primary clarifier	7.81	----	4300	4002	603	1000	500
Anaerobic lagoon	7.41	2583	----	1607	3451	----	----
Ext.anaerobic lagoon	7.41	2411	----	751	1600	----	----
Aerobic lagoon	7.31	2140	----	315	662	----	----
Ext.aerobic lagoon	7.3	2032	----	123	340	----	----
Aeration tank	7.3	1920	----	57	210	----	----
Ext. Aeration tank	7.29	1308	----	27	138	----	----
Settling tank	7.29	1201	----	27	136	----	----
Reverse osmosis plant	7.14	1050	100	6.6	99	300	300

Table 3. Comparison between the findings of the present study & the standards of waste water discharge quality of the treatment plant

Parameter	Untreated Effluent according to KSPCB Standards	Untreated Effluent of the treatment plant	KSPCB tolerance limits for treated effluents for urban re-use	Present findings of the treated effluent plant
pH	6.3-8.3	7.23-7.81	5.5-9.0	7.14
TDS mg/l	275-1120	1920-2846	<2100	1308
TSS mg/l	200-720	100-4300	<100	94
BOD mg/l	50-1900	27-4132	<10	6.6
COD mg/l	50-6000	136-7280	<100	99
Chlorides mg/l	50-350	300-1000	<350	300
Sulphates mg/l	30-400	300-500	<1000	300

Overall Efficiency of the Effluent treatment plant:

This study investigated the treatment efficiency of wastewater treated in phases of the anaerobic, aerobic and reverses osmosis (Table 4). The reverse osmosis gave better removal efficiency of high TDS of 45.31% and BOD of 76% removal efficiency, aerobic treatment showed 59% COD removal whereas anaerobic phase has poor TDS removal capacity (9%). The reverse osmosis gave better removal efficiency of BOD and TDS ,hence this water is used for coolants, boilers, washing of floors and cleaning cellars, packaging, cleaning for each batch , gardening etc.The overall treatment showed good performance. Every treatment phase of this effluent treatment process (ETP) has its unique removal capacity, and the treated water of ETP met the effluent discharged standards of KSPCB and also fulfills the 4Rconcept called Reduce, Reuse, Recycle and Replenish (Desitti *et al.*, 2011).

Table 4. Efficiency of wastewater of the Effluent treatment plant:

Tanks/ parameters	Anaerobic lagoon Efficiency(%)	Ext.anaerobic lagoon Efficiency(%)	Aerobic lagoon Efficiency(%)	Ext.aerobic lagoon Efficiency(%)	Aeration tank Efficiency (%)	Ext. Aeration tank Efficiency (%)	Reverse osmosis plant Efficiency (%)
TDS mg/l	9.0	12.0	19.0	21.33	20.36	39.0	45.31
BODmg/l	60.0	53.0	58.0	60.4	54.4	53.0	76.0
COD mg/l	50.0	54.0	59.0	49.0	39.0	35.0	27.0

Figure .1.Comparison between effluent pH and KSPCB Standards. X-axis which represents treatment plants which includes neutralization tank, equalization tank, Primary clarifier Anaerobic lagoon, Ext.anaerobic lagoon ,Aerobic lagoon ,Ext.aerobic lagoon ,Aeration tank, Ext. Aeration tank ,Settling tank & Reverse osmosis plant

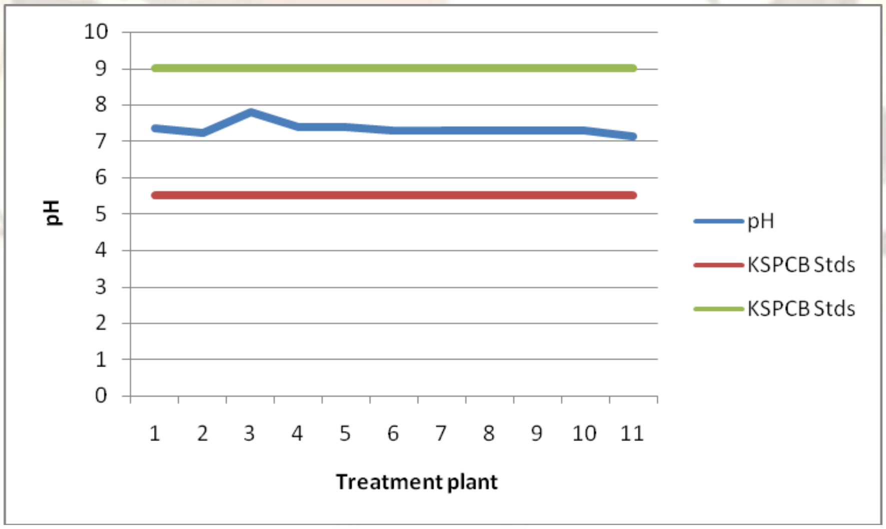


Figure 2. Comparison between effluent COD and KSPCB Standards

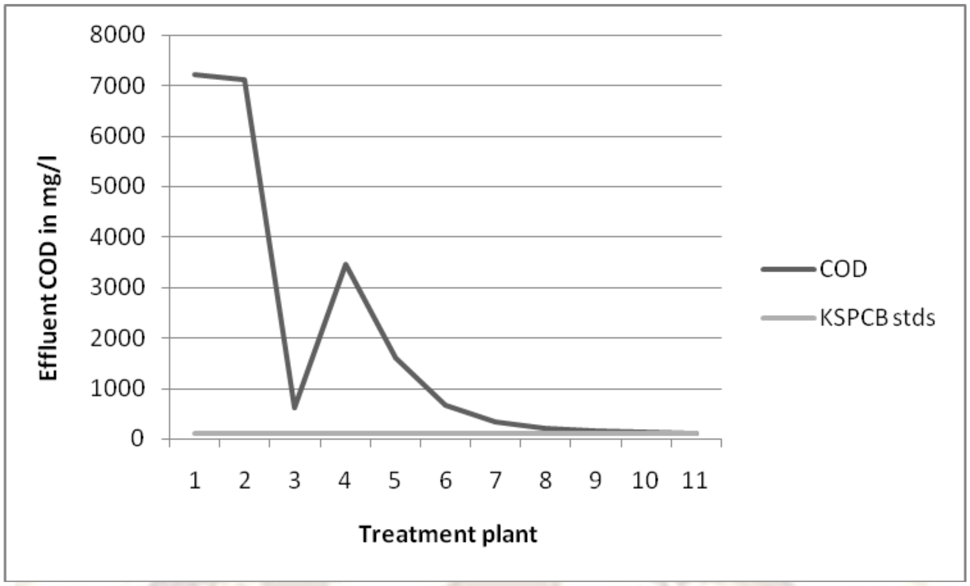


Figure 3. Comparison between effluent BOD and KSPCB Standards

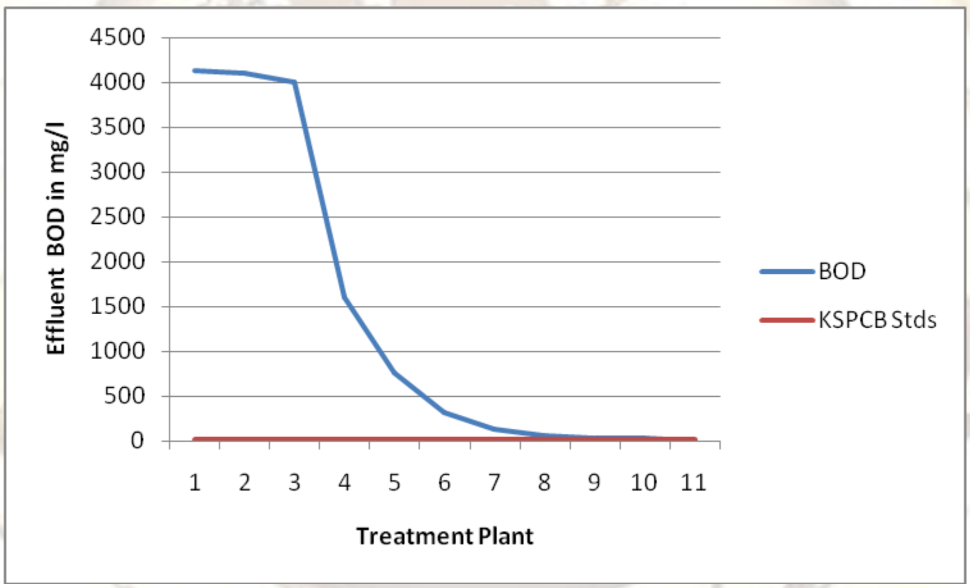
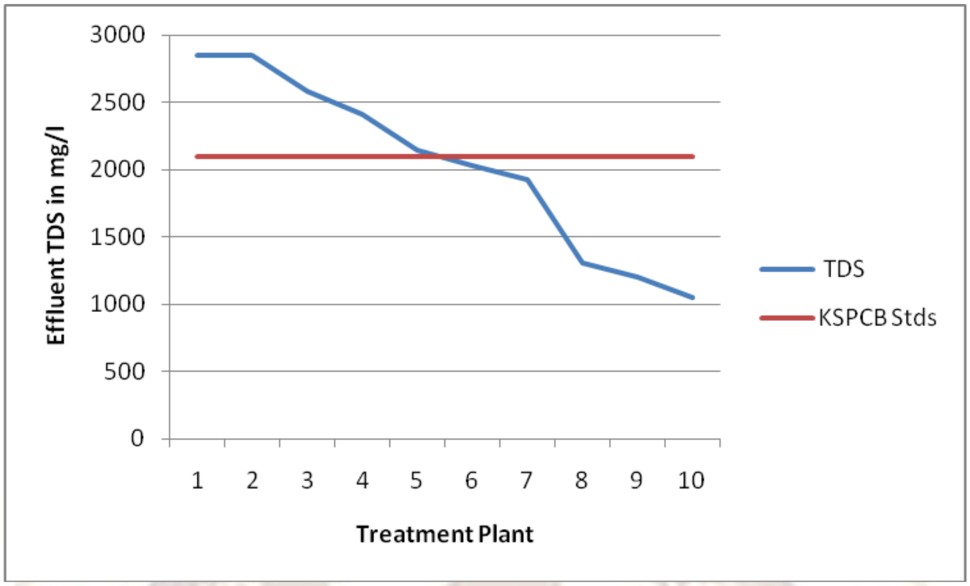


Figure 4. Comparison between effluent TDS and KSPCB Standards



Conclusion:

The performance studies on the pharmaceutical wastewater treatment plant were evaluated. As per available 4months data, behavioral pattern of existing effluent treatment plant appears to be capable of withstanding the shock loads without affecting the efficiency of the plant. The individual units are also performing well and their removal efficiencies are satisfactory. TSS removal efficiencies for the primary clarifiers is 97.8 %,The maximum BOD removal efficiency achieved was 76% & TDS of 45.31% using reverse osmosis process, aerobic treatment showed 59% COD removal whereas anaerobic phase has poor TDS removal capacity (9%-12%)The overall performance of the effluent treatment plant was satisfactory. This treatment plant is high potential for BOD, TSS and TDS removal. Thus this treatment Technology can be considered as a potential plant for industrial wastewater treatment.

Acknowledgement: We would like to thank the management of the pharmaceutical industry for their support and cooperation during the study period.

REFERENCES:

1. Al-Zboon, Kamel and Al-Ananzeh, Nada, (2008), Performance of wastewater treatment plants in Jordan and suitability for reuse, African Journal of Biotechnology., 7 (15), 2621-2629.
2. Ammary B (2007). Wastewater reuse in Jordan: Present status and future plans, Desalination J. Volume 211, Issues 1-3, 10, pp. 164-176.
3. Balasubramian S, Pugalenthi V, Anuradha K,Chakradhar SJ (1999).Characterization of tannery effluents and the correlation between TDS, BOD and COD. Environ. Sci. Health, 34: 4-16.
4. Buzzini AP and Pires EC (2007). Evaluation of an up flow anaerobic sludge blanket reactor with partial recirculation of effluent used to treat wastewaters from pulp and paper plants. Bioresource Technology, 98, 1838-1848.
5. Das P, Das B, Khan YSA (2006). Environmental Assessment of Tannery Wastes from Chittagong, Bangladesh. Asian J. Water Environ. Pollut., 3(1): 83-90
6. Desitti Chaitanyakumar, Syeda Azeem Unnisa, Bhupatthi Rao and G Vasanth Kumar (2011), Efficiency Assessment of Combined Treatment Technologies: A Case Study of Charminar Brewery Wastewater Treatment Plant, Indian Journal of Fundamental and Applied Life Sciences, 1 (2), 138-145.
7. El-Gohary, F. A., Abou-Eleha, S. I. and Aly H. I. (1995). Evaluation of biological technologies for waste water treatment in the pharmaceutical industry. Water Science and Technology.32 (11): 13-20
8. Ernst M, Sperlich A, Zheng X, Ganb Y, Hub J, Zhao X, Wang J, JekelM (2007). An integrated wastewater treatment and reuse concept forthe Olympic Park 2008 Beijing. Desalination J. 202: 3.
9. Hammer MJ (1996). Water and wastewater technol. third edition Prentice –hall. Inc.

10. Garcia, A.,Rivas H. M., Figueroa, J. L. and Monroe A. L. (1995). Case history: Pharmaceutical Wastewater treatment plant upgrade, Smith Kline Beecham Pharmaceuticals Company., Desalination 102(1-3): 255-263.
11. Hashmi Imran (2005). Wastewater monitoring of pharmaceutical industry: treatment and reuse options. Electron. J. Environ. Agric. Food Chem., 4 (4), 994-1004.
12. Haydar S, Aziz JA, Ahmad MS (2007). Biological Treatment of Tannery Wastewater Using Activated Sludge Process. Pak. J. Eng. Appl. Sci., 1: 61-66.
13. Junico M. and Shelef G. (1994). Design operation and performance of stabilization reservoir for waste water irrigation in Israel. Wat. Res. 28: 175-186
14. Kapur, A., Kansal, A., Prasad, R. K. and Gupta, S (1999) Performance evaluation of Sewage Treatment Plant and Sludge bio- methanation, Indian Journal of Environmental Protection, 19. 96 - 100.
15. Kolhe A.S. and V. P. Pawar (2011), Physico-chemical analysis of effluents from dairy industry, Recent Research in Science and Technology, 3(5): 29-32.
16. Khan M. A. and Ahmad S. I. (1992). Performance evaluation of pilot waste stabilization ponds in subtropical region, Wat. Sci. Tech. 26: 1717-1728.
17. Krishanamoorthi S, Sivakumar V, Saravanan K, Prabhu S (2009).Treatment and Reuse of Tannery Waste Water by Embedded System. Modern Appl. Sci., 3(1): 129-134.
18. Larsen T. A., Lienert J., Joss A. and Siegrist H. (2004). How to avoid pharmaceuticals in the aquatic environment. Journal of Biotechnology. 113(1-3): 295-304.
19. K. M. Nazmul Islam, Khaled Misbahuzzaman, Ahmed Kamruzzaman Majumder, Milan Chakrabarty (2011), Efficiency of different coagulants combination for the treatment of tannery effluents: A case study of Bangladesh, African Journal of Environmental Science and Technology , 5(6), 409-419.
20. K. Sundara Kumar et al. (2010), Performance evaluation of waste water treatment plant, International Journal of Engineering Science and Technology, 2(12), 7785-7796.
21. Kaul, S. N., Mukherjee, P. K., Sirowala, T. A Kulkarni, H. and Nandy, T. (1993) Performance evaluation of full scale waste water treatment facility for finished leather industry, Journal of Environmental Science and Health, 28. 1277-1286.
22. Kimura K, Hara H, Watanabe Y., 2005, Removal of pharmaceutical compounds by submerged membrane bioreactors (MBR), Desalination, 178(1–3), pp 135–140.
23. Lübbecke,S., Vogelpohl A. and W. Dewjanin, (1995), Wastewater treatment in a biological high performance system with high biomass concentration, Water Research, 29(3), 793-802.
24. Metcalf & Eddy Wastewater Engineering. Fourth Edition. (International Edition) McGraw-Hill. Singapore. 2003; 611-20.
25. Mohammad Zakir Hossain Khan, Mostafa.M.G (2011), Aerobic treatment of pharmaceutical wastewater in a biological reactor International Journal of Environmental Sciences 1(7).
26. NgMiranda W.J, Yap G. S. and Sivadas M. (1989). Biological treatment of a pharmaceutical wastewater. Biological Wastes. 29(4): 299-311.
27. Overcash M. R. (1986). Techniques for industrial pollution prevention. A compendium for hazardous and non-hazardous waste minimization, Lewis Publishers, Inc., Michigan
28. Puskas K., Essen I. I., Banat I. and Al-Daher R. (1991). Performance of an integrated ponding system operated in arid zones. Wat. Sci. Tech. 23:1543-1542.
29. Pongsak Noophan *et al* (2009) , Nitrogen Removal Efficiency at Centralized Domestic Wastewater Treatment Plants in Bangkok, Thailand , Environment Asia 2 30-35.
30. Rosen M., Welander T., Lofqvist A., and Holmgren J. (1998). Development of a new process for treatment of a pharmaceutical wastewater. Water Science and Technology. 37(9): 251-258.
31. Storhaug, R. (1990) Performance stability of small biological chemical treatment plants, Water Science and Technology, 22. 275-282.
32. Welch E. B. (1980): Ecological effect of wastewater, press syndicate of the University of Cambridge, pp 377
33. Uwadiae S. E, Yerima Y and Azike R.U (2011), Enzymatic biodegradation of pharmaceutical wastewater International Journal of energy and environment 2(4), 683-690.