CLEAN AND LOW COST TECHNIQUES FOR TEXTILE DYE BATH EFFLUENT TREATMENT

By

Saba Sadiq, Dr. Abdullah Yasar and Madiha Zakria

Abstract: Textile is the largest industry of Pakistan. The use of large amounts of dye stuffs during the dyeing stages results in highly colored waste water. The thin layer of discharged dyes formed over the surface decreases the amount of dissolved oxygen. It also reduces photosynthetic activities due to reduced light penetration which badly affects the aquatic flora and fauna. In addition to aesthetic damages to sites, dyes are also toxic and carcinogenic. Conventional methods (activated sludge) and modern techniques (Advance Oxidation Processes) are highly intensive in terms of chemicals, energy and operations.

On the other hand Oxidation Ponds are the simplest aerobic biological treatment processes which require no mechanical aeration. Photosynthesis results in an increase of the dissolved oxygen even beyond saturation levels. It also helps to fix the CO_2 from atmosphere. Algae provide a pathway for the removal of chemical and organic pollutants, heavy metals and pathogens from waste water while producing biomass for bio-fuel production. Solar energy which is abundantly available in Pakistan (throughout the year) can also be used to replace the energy intensive UV system. Solar Assisted Photo Fenton ($FeSO_4$ / H_2O_2) and oxidation ponds can be highly cost effective in comparison to AOP's and activated sludge process by reducing the operational cost especially in the current scenario of energy crises and high prices of electricity.

INTRODUCTION:

Conservation of water resources in order to save the planet and the future of mankind is what we need now. With the growth of mankind, society and technology, the world is reaching to new high horizons but the cost which we are paying for this development is going to be too high. As a result the environmental pollution and the demand for water have increased tremendously. The agricultural, industrial and domestic sectors are consuming 70%, 22% and 8 % of fresh water which results in generation of a number of pollutants. Among these pollutants, the important class of pollutants is dyes [1].

Many industries use dyes in order to color their products such as dyestuffs, textile, paper and plastics. As a result, they generate a considerable amount of colored waste water as shown in figure 1. Colour in water can be recognized even at very low amounts (less than 1 ppm) of dye which is highly undesirable [2].

Fig: 1 Pollution of water bodies caused by Textile industries and Garments factories.

1. Sustainable Development Study Centre GC University Lahore.

The textile industry is one of the greatest consumer of water which is used for dyeing processes i.e. about 100 L of water is used to process about 1 kg of textile materials as a result generates high amounts of effluent. All dyes do not bind to the fabric as high as 50% for reactive dyes as a result 280,000 tons of dyes are discharged every year worldwide which leads to severe contamination of receiving water bodies [3].

Till the late nineteenth century, all the colorants were obtained mostly from natural sources like plants, insects and mollusks and prepared on small scale but after the discovery of first synthetic dye, mauveine in 1856, dyes were manufactured synthetically on a large scale. Dye molecules comprise of two key components: the chromophores, responsible for producing the colour and light absorption in dye molecules, and the auxochromes, which can not only supplement the chromophore but also render the molecule soluble in water and give enhanced affinity (to attach) towards the fibers.

Characteristics of Textile Waste water: The textile waste water consists of untreated dyestuffs and other chemicals that are used in different stages of dyeing, fixing, washing and other processing [4]. The textile waste water is characterized by high Chemical Oxygen Demand (COD), strong colour, high salinity, large amount of dissolved solids and suspended solids [5]. The value of these parameters i.e. COD, Bio-Chemical Oxygen Demand (BOD), Total Suspended Solids (TSS), Total Dissolved Solids (TDS) and heavy metals is very high as compared to the values in National Environment Quality Standards (NEQS) set by the government of Pakistan[6]. The colored waste water has many environmental problems i.e. it affects aesthetics, water transparency. The thin layer of discharged dyes, formed over the surface, decreases the amount of dissolved oxygen and photosynthetic activities due to reduced light penetration which badly affects the aquatic flora and fauna. Furthermore, most synthetic azo dyes are toxic, carcinogenic and mutagenic and pose a potential hazard to human health (Sing et al., 2010). Dissolved solids present in the industry effluents are also a critical parameter e.g., use of common salt and glauber salt etc. in processes directly increase the level of total dissolved solids (TDS) in effluent. TDS are difficult to be treated with conventional treatment systems. Dissolved solids in effluent may be harmful to vegetation and restrict its use for agricultural purpose [7]. In view of the above adverse effects, the textile industry effluent is to be treated and discharged according to the standards prescribed by NEQS.

Waste water Treatment by Traditional Methods: The removal of organic dyes from the waste water is a great challenge for the textile industries, since they are persistent in nature. The traditional methods for removing these dyes by various processes e.g. carbon adsorption, activated sludge treatment, membrane filtration etc. are inefficient, and has further disadvantages of secondary pollutants [8]. In the activated sludge process, the dispersed-growth reactor is an aeration tank or basin containing a suspension of the waste water and microorganisms, the mixed liquor. The contents of the aeration tank are mixed vigorously by aeration devices which also supply oxygen to the biological suspension (Fig. 2 and 3). As aeration is provided mechanically, it increases capital cost of treatment. In this process color is also not removed from industrial wastes and this increases the color through formation of highly colored intermediates through oxidation.

Fig: 2 Industrial Waste water Treatment by Activated Sludge Process

(a)Aeration tank: 1

Aeration tank: 2

(b) Digester Tank (Sludge)

(c) Primary Clarifier

(d) Secondary Clarifier

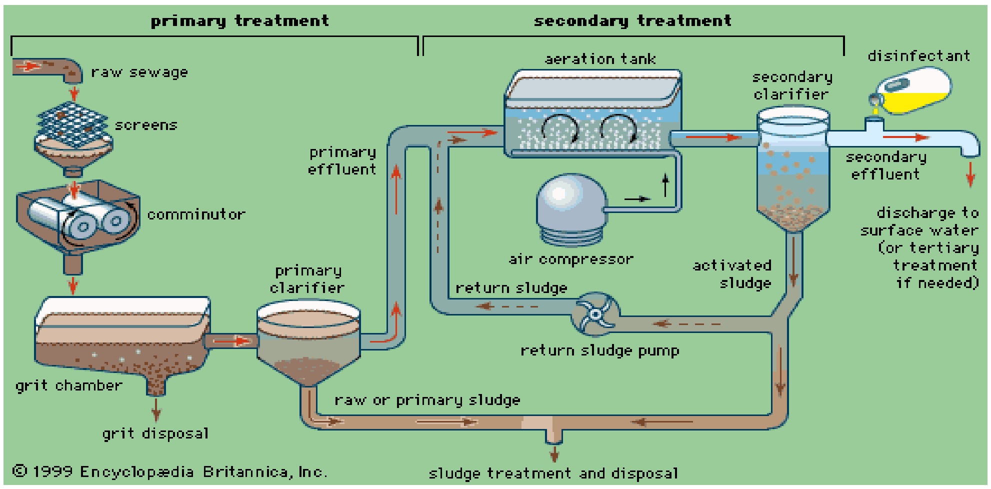

Fig: 3 Schematic Representation of Activated Sludge Process
(**Source:** *Encyclopædia Britannica*, 2011.)

A trickling filter or biofilter consists of a basin filled with support media such as stones, plastic shapes, or wooden slats. Waste water is applied intermittently, or sometimes continuously, over the media. Microorganisms become attached to the media and form a biological layer. Organic matter in the waste water diffuses into the film, where it is metabolized. In the case of Rotating Biological Contractor, the support media is slowly rotating discs that are partially submerged in flowing waste water in the reactor (fig.4 and 5). Oxygen is supplied to the attached bio film from the air when the film is out of the water and from the liquid when submerged, since oxygen is transferred to the waste water by surface turbulence created by the discs' rotation. In both of these reactors the cost of operation and maintenance is very high [9].

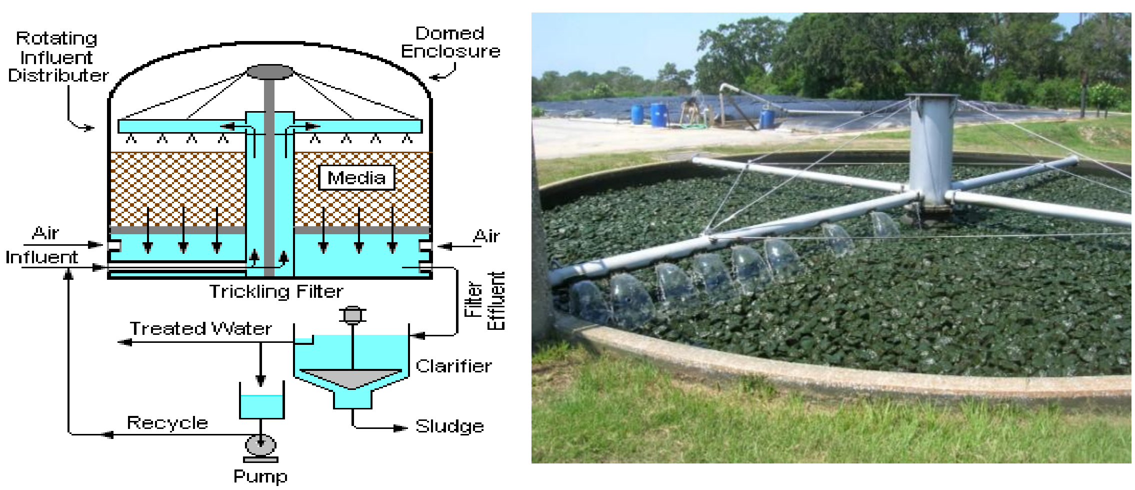

Fig: 4 Waste water Treatment by Trickling Filter.

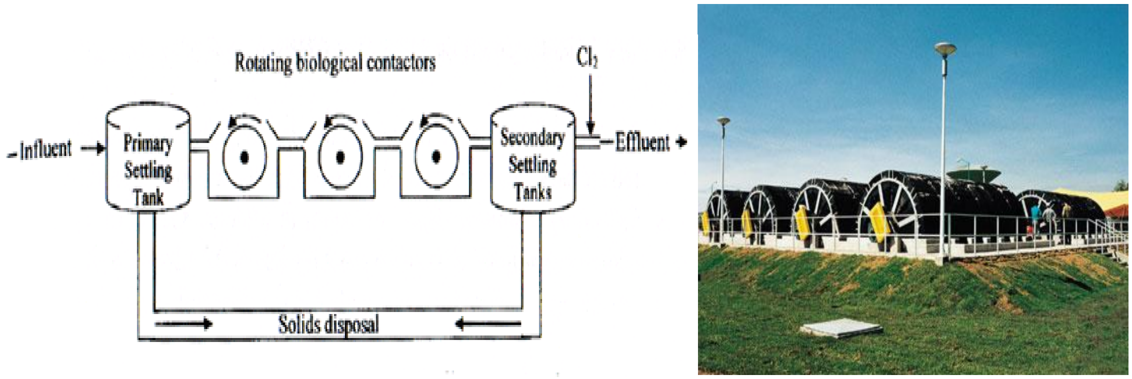

Fig: 5 Waste water Treatment by Rotating Biological Contractor

Algae are very simple chlorophyll-containing organisms composed of one cell or grouped together in colonies. They vary greatly in size (unicellular of 3–10 um (microns) to giant kelps up to 70 m long and growing at up to 50 cm per day (Hillison, 1977). There are two major types of alga: the macro algae (seaweeds) which consist of green algae, brown algae and red algae and occupy the littoral zone, whereas micro algae are found in both benthic and littoral habitats as phytoplankton which comprises organisms such as diatoms (bacillariophyta), dinoflagellates (dinophyta), green and yellow–brown flagellates [10].

Macrophytes are the conspicuous plants such as aquatic angiosperms (flowering plants), pteridophytes (ferns), and bryophytes (mosses, hornworts, and liverworts) that are present in wetlands, shallow lakes, and streams. An aquatic plant can be defined as one that is normally found growing in association with standing water whose level is at or above the surface of the soil [11].

The aquatic microphytes consist of an array of small plants, or algae, which contain chlorophyll and hence are able to produce organic matter through photosynthesis. One of the most important groups is Chlorophyta, green algae which includes algal organisms such as Volvox, Scenedesmus and Pediastrum[12].

Ecosystems dominated by aquatic macrophytes are among the most productive in the world. Aquatic plants possess an outstanding ability for assimilating nutrients and creating favorable conditions for microbial decomposition of organic matter. This ability can be exploited in the restoration process of natural streams, lakes and wetlands, and in waste water treatment systems as shown in fig. 6. Macrophytes based waste water treatment systems have several advantages compared to conventional treatment systems:

- Low operating costs.
- Low energy requirements.
- They can be established at the site where the waste water is produced. [13].

Fig: 6 Treatment of Waste water in ditches planted with (*Scirpus lacustris*) (**Source:** Hans Brix and Hans-Henrik Schierup, 1989)

Conventional Waste Water Treatment Vs Algae-based Waste Water Treatment

1. Cost Effective: Algae-based Waste water Treatment has shown to be a more cost effective way to remove biochemical oxygen demand, pathogens, phosphorus and nitrogen than activated sludge process (Green et al., 1996). Maintenance cost is very low.

2. Low Energy Requirements: Traditional waste water treatment processes involve the high energy costs of mechanical aeration to provide oxygen, whereas in algae based waste water treatment, algae provide the oxygen for aerobic bacteria. Aeration is an energy intensive process, accounting for 45% to 75% of a waste water treatment plant's total energy costs whereas Algae provide the needed oxygen through photosynthesis. For removing one kg of BOD in an activated sludge process, one kWh of electricity for aeration is needed which produces one kg of fossil CO_2 from power generation (Oswald, 2003). By contrast, one kg of BOD removed by photosynthetic oxygenation requires no energy inputs and produces enough algal biomass to generate methane that can produce one kWh of electric power (Oswald, 2003).

3. Reductions in Sludge Formation: Industrial effluents are conventionally treated using a variety of hazardous chemicals for pH correction, sludge removal, color removal and odour removal. Extensive use of chemicals for effluent treatment results in huge amounts of sludge which forms the so called hazardous solid waste generated by the industry and finally disposed by depositing them in landfills. In algae waste water treatment facilities, the resulting sludge with algal biomass is energy rich which can be further processed to make bio fuel or other valuable products such as fertilizers. Algal technology avoids use of chemicals and the whole process of effluent treatment is simplified (fig. 7). There is considerable reduction in sludge formation.

4. The GHG Emission Reduction: The US Environmental Protection Agency (EPA) has specifically identified conventional waste water treatment plants as major contributors to greenhouse gases. Algae based waste water treatment also releases CO_2 but algae consume more CO_2 during its growth than that is being released by the plant, which makes the entire system carbon negative.

5. Production of Useful Algal Biomass: The resulting algae biomass is a source of useful products such as biodiesel [14].

Fig: 7 Algae-based Waste water Treatment

Waste water Treatment by Advanced Oxidation Processes (AOPs):

In recent years, Advanced Oxidation Processes (AOPs) has gained popularity for the degradation of dyes. There are three categories of AOPs: (1) UV/O_3, (2) Photo catalysis (TiO_3 or other semiconductor particles under UV illumination), (3) Fenton Process (Fe^{2+}/ H_2O_2), and Photo Fenton process (Fe^{2+} / H_2O_2 / UV).

Clean and Low Cost Techniques for Textile Waste water Treatment:
On the other hand Solar Assisted Photo Fenton ($FeSO_4/H_2O_2$) and oxidation ponds can be highly cost effective in comparison to AOP's and activated sludge process by reducing the operational cost especially in the current scenario of energy crises and high prices of electricity.

(a)Solar assisted photo Fenton process:
Although a common drawback among AOPs is that large amounts of energy and chemicals are required. It increases the cost of treatment because high energy photons are generated by artificial light. However, photo-Fenton reaction can be driven under solar irradiation with low energy photons in the visible part of the spectrum which reduces the cost [15]. The Fenton reaction is a chemical system which involves hydrogen peroxide and ferrous salts that generates highly reactive hydroxyl radicals, which lead to the oxidation of most organic compounds [16].

Advantages of Solar assisted photo Fenton process:
Fenton's reaction cannot completely degrade organic pollutants and produces substantial Fe^{3+} containing sludge which still requires disposal and further increases treatment cost. Sludge is incinerated to produce power which is not an environment friendly method. Solar assisted photo Fenton process is a potentially powerful method for increasing the treatment efficiency and to reduce the amount of Fe^{3+} containing sludge. When the process uses ultraviolet (UV) radiation and visible light with wave length (λ) less than 450 nm or a combination of both, the process is known as the photo-Fenton process. The photo-Fenton process starts with the combination of H_2O_2 with Fe^{2+} (Eq. (1) :

(1) $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\bullet + OH^-$

When irradiation (λ < 450 nm) is involved, the Fe^{3+} generated by Fenton's reaction (Eq. (1) is continuously reduced to Fe^{2+} as described by Eqs. (2) and (3):

(2) $Fe^{3+} + H_2O \rightarrow Fe(OH)^{2+} + H^+$

(3) $Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + OH\bullet$

Ferrous ions can be regenerated through the use of solar irradiation because there is 20% of solar irradiation with λ < 450 nm which reduces the dosage of Fe^{2+} as shown in fig. 8 [17].

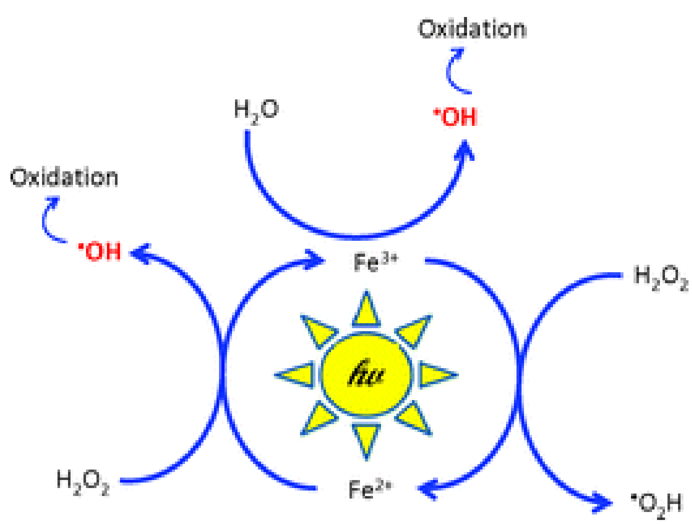

Fig:8 Schematic representation for the coupled Fenton's and photo-Fenton's reactions, where it is evident that the energy supplied increases the catalytic iron cycle, maximizing the free hydroxyl radicals and improving the organic compound oxidation.(**Source:** Melgoza, D., Hernández-Ramírez, A. and Peralta-Hernández, J. M.., 2009).

(b) Algae-based Waste water Treatment (simplest aerobic biological treatment):
Oxidation Ponds are the simplest aerobic biological treatment processes which are used to treat sewage and industrial waste water. The pond effluent consists of bacteria, algae, and soluble organic and inorganic compounds. No mechanical aeration is used, and the aerobic conditions are a result of photosynthetic algae and wind action. They generally are used in rural areas with adequate sunlight, wind action and available land [18]. The treatment of organics will merge as a cost effective and viable option for Pakistan. The use of algae for the treatment of effluent is very efficient in terms of cost and low chemical inputs. Algae are photosynthetic organisms, which are distributed in nearly all parts of the world and in all kinds of habitats .Algae can degrade number of dyes. The ability of degradation depends upon the molecular structure of dyes and the species of algae used [19]. .Algae can remove waste water contaminants such as NH4, NO3, PO4 making algae to grow using these water contaminants as nutrients. They also provide a pathway for the removal of waste water while producing biomass for biofuel production. Photosynthetic algae as a result of photosynthesis eliminate the need for external mechanical aeration [20]. Algae are environment friendly organisms because they feed on CO_2, waste water and in the presence of sunlight (fig. 9). Sun is an infinite and renewable source of energy. Sunlight reaches this earth continuously. According to the data recorded by NASA satellite missions, 1360 watts/m^2 of solar energy reach the top of the earth [21]. Most of this energy is absorbed directly and used to drive the ocean currents and weather; only a fraction (0.1-0.5%) of this is captured by biological systems via photosynthesis which can be utilized to produce biomass [22].

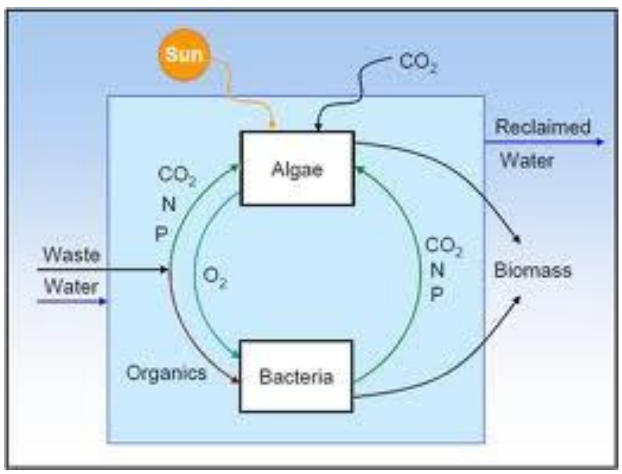

Fig: 9 Schematic representation of the degradation of organic matter with algae.

In recent years, the use of micro algae in bioremediation of colored waste water has attracted great interest in carbon dioxide fixation. The mechanism for the removal of color from dyes can be either biosorption or bioconversion e.g., *Spirogyra* removes the reactive dye (Synazol) from textile waste water by biosorption. Some algae can also breakdown the dyes to simple compounds through bioconversion. Living biomass of macro algae such as *Caulerpa lentillifera* and *Caulerpa scalpelliformis* are also able to remove basic dyes by biosorption. *Chlorella vulgaris* can remove 63–69% of the colour from the mono-azo dye tectilon yellow 2G by converting it to aniline . The use of high rate algae ponds (HRAP) is an efficient approach in bioremediation of industrial waste waters. The system consists of shallow pond with dense algae cultures aerated with paddlewheels. According to Phang *et al*., (2001) Micro algae such as *Chlorella vulgaris* and *Spirulina* grown in HRAP have been shown to be useful in treating rubber effluent and starch factory waste water. In HRAP treating rubber effluent, the productivity of *C. vulgaris* ranged from 25 to 61 g/m^2/day, with high percentage removal of COD, NH_4–N and PO_4–P (Sing et al., 2010).

Many algae displayed their effectiveness in degrading azo dyes present in waste water effluents (Clark and Anliker, 1980; Wang *et al*., 2007; Ertugrul *et al*., 2008). Anon (1977); Jinqi and

Houtian (1992), Acuner and Dilek (2004) stated that some species of *Oscillatoria*, *Chlorella pyrenoidosa* and *Chlorella vulgaris* have degraded azo dyes and decolorized dye waste water. They have also found that some algae can utilize aniline, which is a degradation product of azo dye [23].

The degradation rate of azo dyes by algae was evaluated by Jinqi and Houtian, (1992) and it was found that reduction rate appears to be related to the molecular structure of the dyes and the species of algae used. The algae produces azo reductase enzyme which is responsible for degrading azo dyes into aromatic amine by breaking the azo linkage (-N-N-) that is further metabolised by algae. It is proposed that in stabilization ponds, algae can play a direct role in the degradation of azo dyes, rather than only providing oxygen for bacterial growth [24]. Mohan et al. (2002) studied the removal of Reactive Yellow 22 dye by active *Spirogyra sp*. and reported that algae can remove dyes by biosorption, bioconversion and biocoagulation. While, removal of Acid Red 274 dye using inactivated *Spirogyra rhizopus* system was attributed to biosorption and biocoagulation (Ozer et al., 2006) Dhaneshwar et al. (2007) observed that for microalga *Cosmarium* sp. an increase in pH upto 9 led to 92.4% increase in decolorization rate of Malachite Green. Similarly, Aravindhan et al. (2007) observed that uptake of Basic Yellow dye by *Caulerpa scalpelliformis* increased from 17 to 27 mg/g for an increase in pH from 3.0 to 8.0. The lower pH causes a decrease in color removal efficiency because the H^+ ions compete effectively with dye cations. At higher pH the surface of biomass gets negatively charged which enhances the positively charged dye cations through electrostatic force of attraction [25].

Conclusion

- The effluents from textile industries are a major source of pollution of natural water bodies. Preventive measures must be taken at all levels to prevent water pollution. Effluents should be treated before to be drained in natural water bodies.
- The treatment of textile effluent and sewage with solar assisted photo Fenton (solar/ $FeSO_4/H_2O_2$) system and oxidation ponds will merge as a clean, cost effective and viable option for Pakistan as compared to conventional waste water treatment processes especially in the current scenario of energy crises and high prices of electricity. Treatment of waste water with Oxidation Ponds requires no mechanical aeration and no special skill or expertise for handling than conventional waste water treatment processes. Algal photosynthesis results in an increase of the Dissolved oxygen without the need of aerators and pumps and also helps to fix the CO_2 from atmosphere which causes reduction in greenhouse gases. They utilize natural source of light i.e., sun for algal growth thus they are clean and economically feasible for treating waste water.
- Solar assisted photo Fenton process can be driven under solar irradiation with low energy photons in the visible part of the spectrum which reduces the operational cost of treatment as compared to energy intensive UV system. It increases the treatment efficiency by reducing the amount of Fe^{3+} containing sludge. The treated waste water can be recycled or reuse in industry or for agricultural purposes.

REFERENCES

1. Gupta, V. K. and Suhas. 2009. Application of low-cost adsorbents for dye removal: A review. *Journal of Environmental Management.* **90**(8): 2313–2342.
2. Crini, G. 2006. Non-conventional low-cost adsorbents for dye removal: A review. *Bioresource Technology*. **97** (9): 1061–1085.
3. Ali, H. 2010. Biodegradation of Synthetic Dyes-A Review. *Water Air Soil Pollution.* **213**(1-4): 251–273.
4. Quader, A. K. M. A. 2010. Treatment of textile waste water with chlorine: an effective method. *Chemical Engineering Research Bulletin.* **14**(1): 59-63.
5. Sing, L. L., Chu., W. L. and Phang, S. M. 2010. Use of Chlorella vulgaris for bioremediation of textile waste water. *Bioresource Technology.* **101**(19): 7314–7322.

6. Aslam, M. M., Baig, M. A., Hassan, I., Qazi. I. A., Malik, M. and Saeed, H. 2004. Textile waste water characterization and reduction of its COD and BOD by oxidation. *Electronic Journal of Environmental, Agricultural and Food Chemistry.* **3**(6): 804-811.

7. Mauskar, J. M. 2007. *Advanced Methods for the Treatment of Textile Industries Effluents.* Dr. B. Sengupta, Member Secretary, Central Pollution Control Board, Delhi.p.2.

8. Gomathi, L.D., Kumar, S. G. and Reddy, K. M. 2009. Photo fenton like process Fe^{+3}/ (NH_4) S_2O_8/ UV for the degradation of Di azo dye congo red using low iron concentration. *Central European Journal of Chemistry.* **7**(3): 468-477.

9. http://www.fao.org/docrep/w7241e/w7241e0h.htm.

10. Ali, A. and Gamal, E. 2010. Biological importance of marine algae. *Saudi Pharmaceutical Journal*. **18**(1): 1–25.

11. http://www.eoearth.org/article/Macrophytes?topic=49559.

12. Crafter, S. A., Njuguna, S. G. and Howard, G. W. 1992. **Wetlands of Kenya:** proceedings of the KWWG Seminar on Wetlands of Kenya, National Museums of Kenya. Published by IUCN. Nairobi, Kenya. p. 81.

13. http://mit.biology.au.dk/~biohbn/hansbrix/pdf_files/Ambio_1989_100-107.pdf.

14. http://www.oilgae.com.

15. Torrades, F., Julia, G. M., Jose, A. G. H., Domènech, X. and Peral, J. 2004. Decolorization and mineralization of commercial reactive dyes under solar light assisted photo-Fenton conditions. *Solar Energy.* **77**(5): 573-581.

16. Rossetti, G. H., Albizzati, E. D., Alfano, M. O. 2004. Modeling of a flat-plate solar reactor. Degradation of formic acid by the photo-Fenton reaction. *Solar Energy.* **77**(5): 461–470.

17. Kuo, W. S. and Wu, L. N. 2010**.** Fenton degradation of 4-chlorophenol contaminated water promoted by solar irradiation. *Solar Energy*. **84**(1): 59-65.

18. Robert, N. 1991. *Handbook of Pollution Control Processes.* (1st Ed). Noyes Publishers, New Jersey, USA. p. 251.

19. Khataee, A. R., Zarei, M., Dehghan, G., Ebadi, E. and Pourhassan, M. 2010. Biotreatment of a triphenylmethane dye solution using a Xanthophyta alga: Modeling of key factors by neural network. *Journal of the Taiwan Institute of Chemical Engineers*: 1-7.

20. Munoz, R. and Guieysse, B. 2006. Algal-bacterial processes for the treatment of hazardous contaminants. A Review Water Research.**40** (15): 2799-2815.

21. Quinn, T. J. and Frohlich, C. 1999. Accurate radiometers should measure the output of sun. Nature. **401**:840

22. Whitaker, R. H.and Likens, G. E.1975. The biosphere and man. In: Leith, H., Whitaker, R. H. (Eds.), Primary productivity of the Biosphere. Springer. Berlin, pp. 305-328.

23. Mostafa, M., Sheekhs, E., Gharieb, M. M. and Abou-El-Souod, G.W. 2009. Biodegradation of dyes by some green algae and cyanobacteria. *International Biodeterioration & Biodegradation.* **63**(6): 699–704.

24. Jinqi, L. and Houtian, L. 1992. Degradation of azo dyes by algae. *Environmental Pollution.* **75**(3): 273-278.

25. Srinivasan, A. and Viraraghavan, T. 2010. Decolorization of dye waste waters by biosorbents: A review. *Journal of Environmental Management*. **91**(10): 1915-1929.

26. http://www.probashi.se/indianclothes.php?clothalbum=clothalbum.

27. Activated-sludge method. [Art]. In *Encyclopædia Britannica*.2011. Retrieved from http://www.britannica.com/EBchecked/media/19281/Primary-and-secondary-treatment-of-sewage-using-the-activated-sludge.

28. http://www.bluevistaengineering.com/technical.html.
29. http://www.thewatertreatments.com/waste-water-treatment-filtration-purify-sepration-sewage/trickling-filters-filtration-sewage-treatment.
30. http://www.edie.net/products/view_entry.asp?id=2055.
31. http://water.me.vccs.edu/courses/env110/lesson16.htm.
32. http://www.iwk.com.my/sewerage-fact-02-04.htm.
33. Melgoza, D., Hernández-Ramírez, A. and Peralta-Hernández, J. M. 2009. Comparative efficiencies of the decolourisation of Methylene Blue using Fenton's and photo-Fenton's reactions. *Photochemical & Photobiological Sciences.* **8**(5): 596-599.
34. http://marketplayground.com/forum/showthread.php/808-Algae-Information-Production-Methods-and-Terminology/page2.