



A comparative study on the treatment methods of textile dye effluents

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ABSTRACT

Textile and dyeing industries are responsible for contaminating water due to discharge of coloured effluents. So water pollution due to colour from textile and dyestuff industries is a topic of major concern of scientist today. The removals of dyes present in these industrial effluents have been received great potential in last few years. It is due to increasing environment awareness and implementation of ever strict environmental rules. These textile effluents are highly toxic as they contain a large no of metal complex dyes. These high concentrations of dyes causes may water borne diseases and increase the BOD level of receiving water. In the present paper various methods of treatment of textile effluent have been studied and discussed to find out effective treatment of textile effluents. In present years colour effluents is treated by so many techniques like Chemical oxidation, Ozonation, Ion exchange process, Electrochemical process, Electrolytic precipitation, Foam fractionation, membrane filtration, photo catalytic degradation, Adsorption. From the study it has been found that no single method is sufficient to control the water pollution by textile effluents, however all the above mentioned methods minimize the percentage of colour and other parameters in textile effluents. Out of which adsorption process has been found to be more effective method for treating dye-containing textile effluents economically.

Keywords: adsorption, azo dyes, low cost adsorbent, textile effluent.

INTRODUCTION

Water pollution due to color dyestuff industries is topics of major concern today. Many industries use dyes extensively in different operation such as textile, paper, plastic, leather, tanning etc. these industries discharge verity of pollutants in different process. Out of which Textile industries discharge large quantity of dyes into water bodies, poses serious ecological problems. In recent years different approaches have been discussed to tackle man made environmental hazards.

Textile Engineering has direct connection with environmental aspects to be explicitly and abundantly considered. The main reason is that the textile industry plays an important role in the country like India and it accounts for around one third of total export. Out of various activities in textile industry, they discharge a large variety of dyes and chemicals addition that make the environmental challenge for textile industry not only as liquid waste but also in its chemical composition. Main pollution in textile wastewater came from dyeing and finishing processes. These processes require the input of a wide range of chemicals and dyestuff, which is generally are organic compound of complex structure. Because all of them are not contained in the final product, become waste and it affect the aquatic ecosystem in number of ways such as depleting the dissolved oxygen content or settlement of suspended substances

in aerobic as well as anaerobic condition. The major pollutants in textile waste water are high suspended solid, COD, heat, color, acidity and other soluble substances, Most dyes used in textile industries are stable to light and not biologically degradable. Further more, they are resistant to aerobic digestion. Dyes usually have a synthetic origin and complex aromatic molecular structures which make them more stable and more difficult to biodegrade. Today there are more than 10,000 dyes available commercially and over 7×10^5 tons are produced annually worldwide^[28]. It was estimated that about 12-15% of these dyes are released in effluents during processes, causes environmental pollution. These colored compounds are not only aesthetically displeasing but they also inhibit sunlight from penetrating into the stream and reduce the photosynthetic reaction some dyes are also toxic and carcinogenic^[8].

Thus, a study on different measures, which can be adopted to treat the wastewater discharged from textile chemical processing industries to protect our surroundings from possible pollution problem, has been the focus point of many recent investigations.

EXPERIMENTAL SECTION

Methods of textile effluent treatment

The effluent treatment method is broadly classified into three main categories: physical, chemical, and biological treatments. There are four stages, preliminary, primary, secondary, and tertiary treatments to treat the textile effluents. The preliminary treatment processes are equalization and neutralization. The primary stages involve screening, sedimentation, floatation, chemical coagulation and flocculation. Secondary stages are used to reduce the organic load, facilitate physical / chemical separation and biological oxidation. Tertiary stages are important because they serve as polishing of effluent treatment^[3].

2.1 Preliminary treatment

The conventional treatment systems like physico-chemical treatment followed by biological treatment are installed in majority of textile industries. The first step in the wastewater treatment is to mix and equalize the wastewater streams that are discharged at different time, and different intervals from different stages in processes. Equalization ensures that the effluent have uniform characteristic in terms of pollution load, pH and temperature^[3]. Some success has been achieved in the recovery of some textile inputs, and this method, will further solve problem faced in the area of waste reduction. The scheme given in figure-1 describes this procedure.

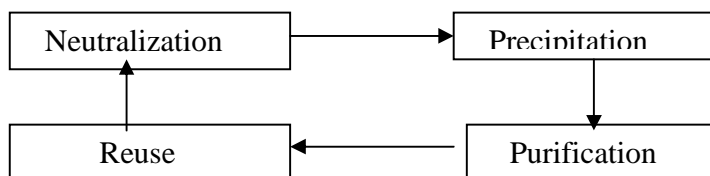


Figure-1: Preliminary treatment

Primary Treatment

The primary treatment involves screening, sedimentation, floatation, but after the treatment of effluents by above processes some fine or suspended and colloidal particles cannot be efficiently removed. In such cases mechanical flocculation or chemical coagulation is employed.

In chemical coagulation the effluent is then subject to flash mixing for the addition of coagulants such as lime

$[\text{Ca}(\text{OH})_2]$, alum, ferrous sulphate (FeSO_4), ferric chloride (FeCl_3), polyelectrolyte and processed through clariflocculator or flocculator and settling tank. Selections of appropriate coagulants doses of chemicals are determined on the basis of treatability study of effluent samples. The chemical treatment helps in reduction of color and suspended solids. A significant reduction in BOD and COD value is also observed. Chemical coagulation process effectively decolorizes insoluble dyes, but it fails to work well with soluble dyes.

2.3 Secondary treatment

In secondary treatment, the dissolved and colloidal organic compounds and color present in wastewater is removed or reused and to stabilize the organic matter. This is achieved biologically using bacteria and other microorganisms. These processes may be aerobic or anaerobic.

In aerobic processes, bacteria and other microorganisms consume organic matter as food. They bring about the following sequential changes:

1. Coagulation and flocculation of colloidal matter
2. Oxidation of dissolved organic matter to carbon dioxide.
3. Degradation of nitrogenous organic matter to ammonia, which is then converted into nitrite and eventually to nitrate.

Anaerobic treatment is mainly employed for the digestion of sludge. The efficiency of this process depends upon pH, temperature, waste loading, absence of oxygen and toxic material. However aerobic treatment of azo dye waste has proven ineffective in most cases but is often the typical method of treatment used today^[21].

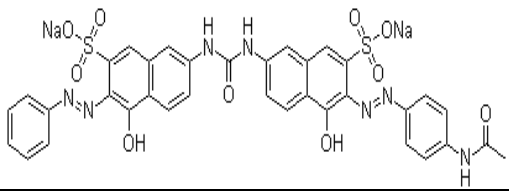
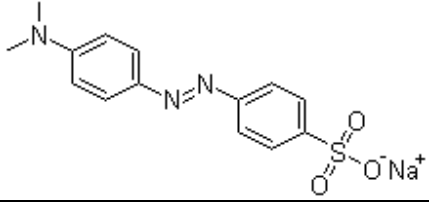
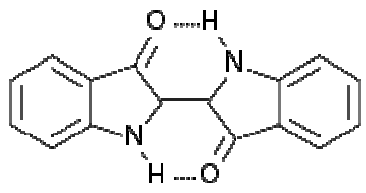
It is worthwhile to mention that the textile waste contains significant quantities of non-biodegradable chemical polymers. Since these conventional treatment systems are not very effective in removal of pollutants such as dissolved solids, color, trace metals etc.

There is the need for efficient tertiary treatment process.

2.4 Tertiary Treatment

Textile effluents may require tertiary or advance treatment methods to remove particular contaminant like various type of dyes such as Congo Red (CR), Methyl Orange (MO), Methylene blue, C.I. Direct red 80 (DR), C.I. Reactive Red 17 (RR), C.I. Direct Yellow 50 (DY), Direct Red 23 etc. or to prepare the treated effluent for reuse. Some common tertiary operations are removal of residual organic colour compounds by adsorption and removal of dissolved solids by membrane filtration. The wastewater is also treated with ozone (O₃) or other oxidizing agent to destroy many contaminants. Evaporation and crystallization are other methods to minimize effluent disposal problems. Table 1 shows that the structures and molecular formulas of various azo dyes.

Table 1: Structure and molecular formula of some azo dyes

Dye	Structure	Molecular Formula
Direct Red 23		C ₃₅ H ₂₅ N ₇ Na ₂ O ₁₀ S ₂
Methyl Orange		C ₁₄ H ₁₄ N ₃ NaO ₃ S
Indigo		C ₁₆ H ₁₀ N ₂ O ₂

Advance methods for treatment

3.1 Chemical oxidation

This is the most commonly used method for decolourisation by chemical means. This is adopted mainly due to its simplicity of application. The main oxidizing agents are Ozone (O₃), hydrogen peroxide (H₂O₂) and UV irradiation. Combination of these oxidizing agents showed the greatest promise to treat textile wastewater. These oxidants effectively decolorized dyes, however did not remove COD completely. Oxidation processes are characterized by production of OH[•] radicals and generation of OH[•] is commonly accelerated by combining O₃, H₂O₂, TiO₂, UV radiation, electron-beam irradiation and ultra sound of these O₃/H₂O₂, O₃/UV and H₂O₂/UV hold the greatest promise to oxidize textile wastewater^[5,12,25,1]. Chemical oxidation removes the dye containing effluent by oxidation in aromatic ring cleavage of the dye molecules. This process is effective but oxidant requirement are very high and expensive^[26].

3.2 Ozonation

It is a very good oxidizing agent due to its high instability (oxidation potential 2.07) compared to chlorine (Cl) another oxidizing agent, and H₂O₂. Oxidation by Ozone (O₃) is capable of degrading chlorinated hydrocarbon, Phenols, Pesticides and aromatic Hydrocarbon. Ozonation leaves the effluent with no color suitable for discharge into environmental wastewater. A major disadvantage of Ozonation is its short half-life, typically being 20 min; this can be further shortened if dyes are present, with stability being affected by the presences of salts, pH and temp. In alkaline condition, O₃ decomposition is accelerated, and so careful monitoring of the effluent pH is required^[2]. Table-2 shows that the effect of ozonation on textile effluent and Figure-2 shows the graphical effect of ozonation on textiles.

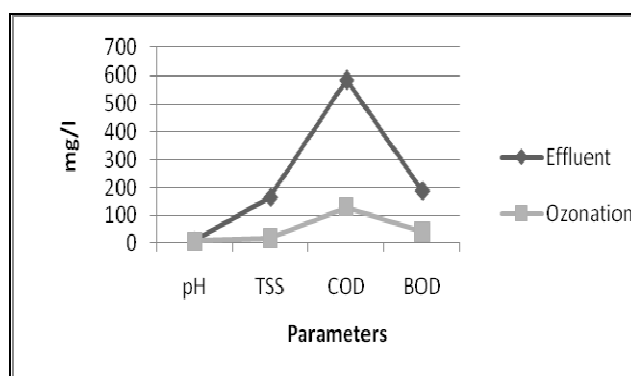


Figure2: Graphical representation of ozonation on Textile effluents

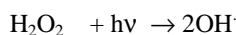
Table 2: Effect of ozonation on textile effluent

S.No	Parameter	Effluent	Ozonation
1.	pH	9.88	6.92
2.	TSS	167	19
3.	COD	586	130
4.	BOD	190	41
5.	Color %	< 10	Colorless

3.3 Photochemical Process

This method degrades dye molecules into carbon dioxide and water by UV treatment. Degradation is caused by the production of high concentrations of hydroxyl radicals. UV light may be used to activate chemicals, such as H₂O₂ and the rate of removal is influenced by the intensity of the UV radiation, pH, dye structure and the dye bath composition. The Photo oxidation of a chlorotriazine reactive azo dye, Reactive Orange 4 has been carried out in the presence of H₂O₂ using UV Rays. The advantages of photochemical treatment of dye containing effluents are: no

sludge is produced and foul odours are greatly reduced. UV light activates the destruction of H₂O₂ into two OH radicals.



3.4 Ion exchange process

Ion exchange has not been widely used for the treatment of dye-containing effluents, mainly due to the opinion that ion exchangers cannot accommodate a wide range of dyes. Wastewater is passed over the ion exchange resin until the available exchange sites are saturated. Both cationic and anionic dyes can be removed from dye-containing effluent in this way. Advantages of this method are no loss of absorbent on regeneration; reclamation of solvent after use and the removal of soluble dyes and the major disadvantage is its high cost. This method is not effective for disperse dyes.

3.5 Electro Chemical Process

The Electro Chemical Processes have found used in destruction of toxic and non-biodegradable organic matter by direct or indirect oxidation/reduction. These methods are very promising as they involve the controlled degradation of the pollutants. They are moreover very effective towards reduction of chromophoric groups of dyes and color removal, which is the main disturbing factor for water recycling in most of the industries^[10]. Table 3 shows that the effect of electrochemical treatment on textile effluent and Figure-3 shows graphically the effect of electrochemical treatment on textile effluent.

S. No	Textile Effluent	Before Treatment (ppm)	After Treatment (ppm)
1	COD	246	73.9
2	TDS	243.5	71.7

Table 3: Characteristic of electrochemically treated effluent

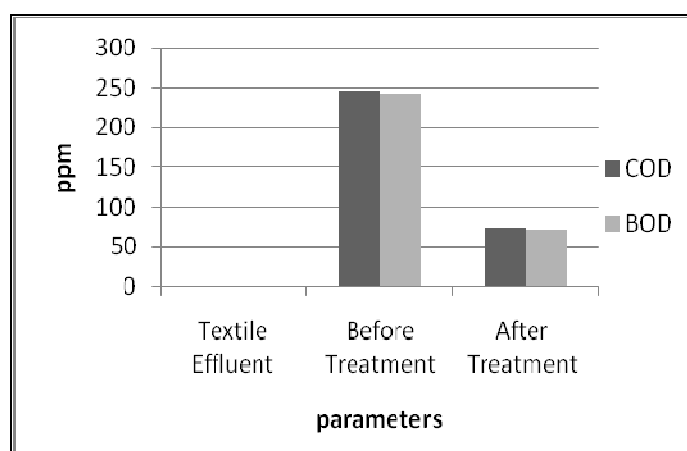


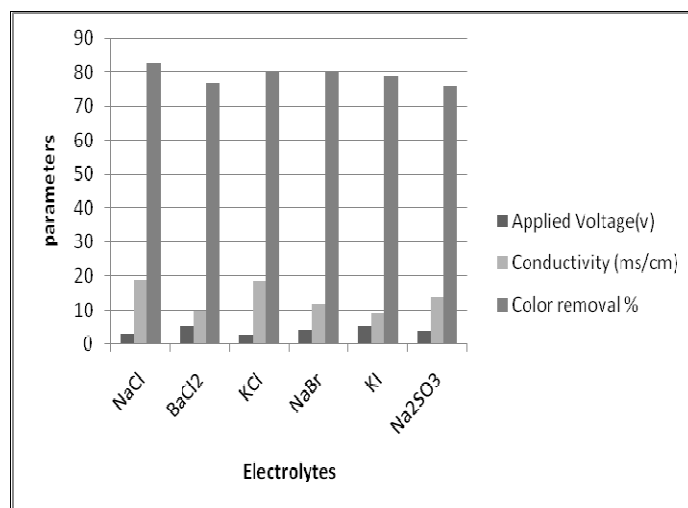
Figure 3: Effect of electrochemical treatment on textile effluent

3.6 Electrolytic precipitation & Foam fractionation

The electrolytic precipitation process is highly dependent on the chemistry of the wastewater, especially its conductivity. In addition other characteristic such as pH, particle size and chemical constituent influences the process. Table 4: shows that the type of electrolytes don't have any important effect against color removal percent, but in contrast of applied voltage and conductivity of solutions contains each of electrolytes (10 g/l), it can be shown that NaCl with higher color removal percent (83%) is the best electrolyte because it is cheap and the solution contains it has high conductivity (19.13 ms/cm) thus it need low voltage for electro coagulation (2.9V) and so it is economical in industrial scale^[11]. Foam fractionation is experimental method based on the phenomena that surface-active solutes collect at gas-liquid interfaces. However, the chemical costs make this treatment method too expensive^[27]. Figure-4 shows the comparison between different electrolytes.

Table 4: Characteristic of different electrolytes

Type of electrolytes	Applied Voltage(v)	Conductivity (ms/cm)	Color removal %
NaCl	2.9	19.13	83
BaCl ₂	5.1	9.67	77
KCl	2.7	18.75	80
NaBr	4.2	11.77	80
KI	5.3	9.18	79
Na ₂ SO ₃	3.8	13.8	76

**Figure 4: Comparison between different electrolytes**

3.7 Membrane filtration

This method has the ability to clarify, concentrate and most importantly, separate dye continuously from effluent. It has some special features unrivalled by other methods; resistance to temperature, an adverse chemical environment and microbial attack. The concentrated residue left after separation, poses disposal problems and high capital cost, and possibility of clogging and membrane replacement are its disadvantages^[15].

This method of filtration is suitable for water recycling within a textile dye plant, if the effluent contains low concentrations of dyes, but it is unable to reduce the dissolved solid content, which makes water re-use a difficult task.

3.7.1 Ultra filtration

Ultra filtration membranes retain only macromolecules and suspended solids. Thus salts, solvents and low molecular weight organic solutes pass through ultra filtration membrane with the permeate water. Since the membrane does not retain salts, the osmotic pressure differences across ultra filtration membrane are negligible. Flux rates through the membranes are fairly high, and hence lower pressures can be used.

Ultra filtration membranes may be made from cellulose acetate, polyelectrolyte complexes, nylon and inert polymers. Hence, acidic or caustic streams may also be processed and the process is not usually limited by chemical attack of the membranes^[15].

3.7.2 Nanofiltration

Nanofiltration is essentially a lower pressure version membrane where the purity of permeates water less important. This process is used where the high salt rejection of reverse osmosis is not necessary. The nanofiltration is capable of removing hardness elements such as calcium or magnesium together with bacteria, viruses, and colour. Nanofiltration is preferred when permeate with TDS but without colour, COD and hardness is acceptable^[27]. Table 5 shows that the comparison between ultrafiltration and nanofiltration.

Table 5: Comparison between different membrane filtration

Process	Pore size	Molecular Wt.	Uses for removal of
Ultrafiltration	0.002-0.10	1000-200000	Colloids, Virus, Protein
Nanofiltration	0.001-0.07	180-15000	Dyes, Pesticides, divalent ions etc.

3.8 Photo catalytic degradation

An advanced method to decolorize a wide range of dyes depending upon their molecular structure^[21]. In this process, photoactive catalyst illuminates with UV light, generates highly reactive radical, which can decompose organic compounds. Photocatalytic degradation by semiconductor is a new, effective and rapid technology for the removal of pollutant from water^[17]. Recently TiO₂ and ZnO have been used as effective and nontoxic semiconductor photo catalysts for the degradation of wide range of organic chemicals, synthetic dyes as well as super hydrophilic and anti bacteria properties^[16]. Solar UV-Light reaching the surface of the earth and available to excite TiO₂, and UV active photo catalyst, is relatively small and also artificial UV light source are somewhat expensive^[7]. ZnO appears to be a suitable alternative to TiO₂. This photo catalyst, but most of the semiconductor have poor activity when used alone.

3.9 Adsorption

Various techniques have been employed for the removal of dyes from wastewater. Activated carbon has long been used as a standard adsorbent for color removal. In spite of its importance in various cleaning procedures activated carbons remain expensive; therefore the development of low cost alternative adsorbent has been the focus of recent research.

Many researchers have used agriculture waste such as banana & orange peel^[4], wheat straw^[22], sugar cane dust, saw dust, rice husk^[13] waste mud^[18] & wood materials^[14], cotton, bark, hair, coal, sewage sludge based activated carbon, coir pith^[19], almond shell, walnut shell^[6], fly ash, bottom ash, soil^[20] etc. as adsorbent which remove dye from colored effluent economically. However the existing wastewater technology i.e. adsorbent is often inadequate to control the color of effluent and toxicity of wastewater to aquatic organism. Table 6: shows that the comparative study of different adsorbents and their adsorption capacity^[9].

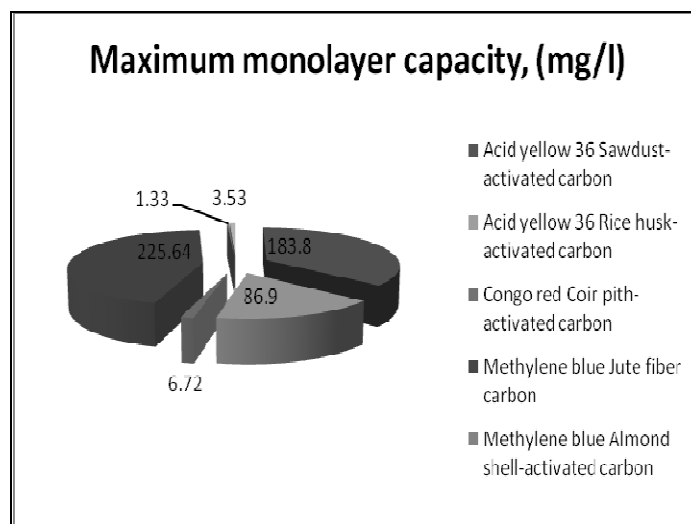


Figure 5: Comparison of the maximum monolayer adsorption of some dyes onto various adsorbents

Table 6: Comparison of the maximum monolayer adsorption of some dyes onto various adsorbents

Dyes	Adsorbent	Maximum monolayer capacity, (mg/l)
Acid yellow 36	Sawdust-activated carbon	183.8
Acid yellow 36	Rice husk- activated carbon	86.9
Congo red	Coir pith- activated carbon	6.72
Methylene blue	Jute fiber carbon	225.64
Methylene blue	Almond shell-activated carbon	1.33
Methylene blue	Walnut shell-activated carbon	3.53

CONCLUSION

On studying various methods of effluent treatment it is clear that not a single treatment, either primary, Secondary or tertiary treatment is sufficient to control the impurities up to the level of permissible limits, because all of these methods suffer from one or other limitations and none of them were successful in removing the color from wastewater most of the treatments are very expensive, and not very much successful in treatment of effluents but out of which adsorption process has been found to be more effective method for treating dye containing effluents economically.

REFERENCES

- [1] A.K. Adel, I. Azni, S. Katayon, and T.G. Chuah, **2004**, *Global Nest: the Int. J.* Vol 6, No3 : 222-230.
- [2] B. Ahmet, Y. Ayfer, L. Doris, N. Nese, and K. Antonius, **2003**, *Dyes and Pigments* 58: 93-98.
- [3] V.O. Ajibola, **2001**, *Journal of scientific Industrial Research*, Vol.60: 735-737.
- [4] G. R. Annadurai, Juang, and D. Lee, **2002**, *Journal of Hazardous Material*, B92: 263-274.
- [5] I. Arslan, I.A. Balcioglu, and D.W. Bahnemann, **2000**, *Dyes and Pigments* 47: 207-218.
- [6] A. Aygun, S. Yenisoay-Karakas, and I. Duman, **2003**, *Microporous Mesoporous Meter* 66: 189-95.
- [7] B. Pare, P.Singh, and S.B. Jonnalagabba, **2008**, *Indian Journal of Chemistry*, Vol. 47: 830-835.
- [8] R. Gong, M. Li. C. Yang, and Y. Sun, Chen, **2005**, *Journal of Hazardous Materials*, B121: 247-250.
- [9] B.H. Hameed, A.L. Ahmad, and K.N.A. Latiff, **2007**, *Dyes and Pigments* 75:143-49.
- [10] R. Jain, N. Sharma, and M. Bhargava, **2004**, *Journal of scientific Industrial Research*, Vol. 63: 405-409.
- [11] M. Kashefialast, M. Khosravi, R. Marandi, and K. Seyyedi **2006**, *International Journal of Environmental Science and Technology* Vol. (4): 365-371.
- [12] S. Libia, J. Claudia, and N.K. Santosh, **2001**, *Water Research* 35: 2129-2136,
- [13] P.K. Malik, **2003**, *Dye and Pigments* 56: 239-49.
- [14] G. McKay, and V.J.P. Poots, **1980**, *Journal of Chemical Technology and Biotechnology* 30: 279-292.
- [15] Mehta, and Soham. **2003**, *Environnemental Pollution Control Journal* Vol. 6: 14– 19.
- [16] V. Mirkhani, S. Tangestaninejad, M. Moghadam, M.H. Habibi, and A.Rostami- Vartooni, **2009**, *Journal of the Iranian Chemical Society*, Vol.6 (3): 578-587
- [17] Mohamod Sleiman, Vildoza, Daniel Ferronato, Corinne Chovelon, and Jean-Marc, **2007**, *Applied Catalysis B: Environmental*, 77 (1-2): p.1
- [18] C. Namasivayam, and S.E. Arasi, **1997**, *Chemosphere* 34(2): 401-417.
- [19] C. Namasivayam, and D. Kavitha, **2002**, *Dye and Pigments* 54: 47-58.
- [20] M.F.R., Pereira, S.F. Soares, J.J.M. Orfao, and J.L. Figueiredo, **2003**, *Carbon* 41: 811-821.
- [21] B. Smith, G. Neal, H. Boyter, and J. Piszczek, **2007**, *Journal of Chemical Technology & Biotechnology*, Vol.82(1): 16-24
- [22] T. Robinson, B. Chandran, and P. Nigam, **2001**, *Water Res* 36: 2824-2830.
- [23] M.R. Sampath, **1993**, *Colourage*: 37-40
- [24] S. Senthikumar, P.R. Varadarajan, K. Porkodi, and C.V. Subburaam, **2005**, *Journal of Colloid Interface Science* 284: 78-82.
- [25] L. Stanislaw, S. Monika, and Z. Renata, **2001**, *Journal of Biotechnology* 89: 175-184.
- [26] T.R. Sundararaman, V. Ramamurthi, and N. Partha, **2009**, *Journal CCSE Modern Applied Science*. Vol.3 (8): 881- 886
- [27] Yazhen, Xu, Remi, E. Lebrun, P.J. Gallo and P. Blond, **1999**, *Journal of Separation Science and Technology*, Vol. 34: 2501-2519.

[28] S.Wang, Y. Bonjoo, and A. Choueib, **2005**, *Chemosphere* 60: 1401-1407.