Adsorptive Removal of Congo Red and Sunset Yellow Dyes from Water Systems by Lady Finger Stem

[1]AADIL ABBAS, [2]RABIA REHMAN*, [1]SHAHZAD MURTAZA, [3]UMER SHAFIQUE, [2]AMBREEN ZAHID AND [1]RABIA AYUB
[1] *Department of Chemistry, University of the Gujrat, Gujrat, Pakistan.*
[2] *Institute of Chemistry, University of the Punjab, Lahore-54590, Pakistan.*
[3]*Center for Undergraduate Studies, University of the Punjab, Lahore-54590, Pakistan.*
grinorganic@yahoo.com*

(Received on 30th January 2012, accepted in revised form 12th May 2012)

Summary: In this research work two anionic dyes, i.e. Congo Red and Sunset Yellow were removed successfully from aqueous media by Lady Finger stem in batch mode. Operational conditions optimization showed that agitation speed and particle size did not affect much in adsorption of these dyes; but contact time, pH, adsorbent dose and temperature of system effects the adsorption rate. Optimized conditions of adsorption for Congo Red dye were: 40 minute contact time, 8.0 pH, 0.5 g adsorbent dose, 40-60 microns mesh sized particles, 150 rpm agitation speed and 50 ºC temperature. Whereas for Sunset Yellow optimized conditions were: 30 minute contact time, 2.0 pH, 2.5 g adsorbent dose, 20-40 microns mesh sized particles, 50 rpm agitation speed and 30 ºC temperature. Suitability of equilibrium data was modulated with Langmuir, Freundlich and Temkin models and found that both physiosorption and chemisorption processes play important role in adsorption of these dyes by Lady Finger stem. The results demonstrated that Lady Finger stem can be efficiently employed on larger scale wastewater treatment.

Keywords: Congo Red, Sunset Yellow, Anionic dyes, Lady Finger stem, Adsorption, Isotherm.

Introduction

Dyes are widely used in textile industry, paper printing, leather tanning and dyeing, food additives, paint and decorative glass industries. In most of the applications more than 50 % of the dye used is usually lost in wastewater. Various types of inorganic and organic substances are used for dyeing. Organic dyes are generally difficult to treat, because their decomposition produces hazardous metabolites and products. These dyes are generally classified into cationic, anionic and non-ionic types on the basis of their hydrolysis reaction products. Anionic dyes are mostly direct azo-dye, usually soluble in water. In this study, two anionic dyes were used namely Congo Red and Sunset Yellow. Their structures are given in Fig.1 and 2 respectively [1].

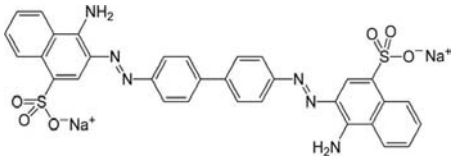

Fig. 1: Molecular structure of Congo Red dye.

Congo Red is commonly used as an indicator of pH and in histological staining for amyloid. It is also used in textile dyeing and as a laboratory aid for free hydrochloric acid in gastric contents testing. The color of Congo Red changes from dark blue at pH 2.0 –4.0 to red at pH 12.0. It is hazardous in nature due to its mutagenic and carcinogenic metabolites which can severely damage reproductive systems of organisms. It has very irritating and rational effects on skin, eyes and gastrointestinal tract. It affects blood clotting and induces drowsiness along with respiratory tract infections [2-4]. Whereas Sunset Yellow is disodium salt of 6-hydroxy-5-[(4-sulfophenyl) azo]-2-naphthal-enesulfonic acid. As food additive it is marketed as E110. It is usually used to impart reddish-yellow color in medicinal applications: like tablets, syrups and capsules; and in toothpastes, hair rinses, carbonated beverages, cereals, canned foods and cosmetics in order to enhance the natural colors which are destroyed during processing or storage of these items. Its excess in food stuff leads to hazardous effects like headache, nausea and hyperac-tivity which sometimes may lead to cancer [5-7]. So, there removal from waste water is crucial before dumping them into main water streams.

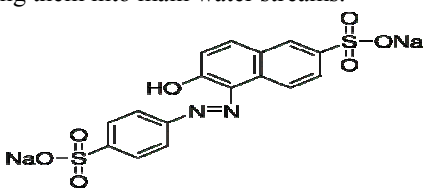

Fig. 2: Molecular structure of Sunset Yellow.

*To whom all correspondence should be addressed.

Several ways are adopted for wastewater treatment for the removal of dyes like catalytic oxidation, photo-catalytic decolorization, ozonation, coagulation, electrolysis, biological degradation and adsorption on activated charcoal. In recent years, several studies carried out to evaluate the adsorption capacity of various agro-waste materials for removing dyes on laboratory scale like: orange peel, pine cone, mango seeds, almond shell, tea waste, lemon peels, banana pith, cotton waste, neem leaves, bamboo dust, coconut shell, rose wood, peanut hull, groundnut shell, rice husk and straw, gram husk, bagasse fly ash, pomegranate peel, Radish peels, Jamun stem, pistachio hull and sawdust [1, 8-25].

In present research work, Lady Finger (Botanical name: *Abelmoschus esculentus*, Local names: Okra, Gombo, Bhindi, Dherosh) stem is used as an adsorbent for removing Congo Red and Sunset Yellow dye from water. Its hollow stem is not so hard, but due to its coarse texture and sour taste, it cannot be used as fodder for animals [26, 27]. That is why; its adsorption capacity has been investigated for making this agro-waste a valuable material for wastewater treatment.

Results and Discussions

Surface Characterization of the Adsorbent

Surface characterization of Lady Finger stem was carried out by recording its FT-IR spectrum and resulting characteristic peaks were given in Table-1. It shows that different functional groups like alkenes, aromatic rings, ester, ketone and alcohol are present in the adsorbent which can interact with dyes during chemisorption process [28].

Study of Factors Effecting Adsorption Rate

Several factors involved in determining the rate of adsorption in various ways. They are studied and described here for adsorption of Sunset Yellow and Congo Red dyes by Lady Finger stem by varying them one at a time while others keeping constant. The results are shown in Figs. 3-8.

1. Effect of Contact Time

The dynamics of adsorption is strongly dependent on contact time interval between adsorbent and adsorbate. For this purpose, optimization of contact time interval conditions between Lady Finger stem and dye solutions were carried out in batch mode keeping other factors constant and results are shown in Fig. 3. It was observed that a rapid adsorption occurred for sunset yellow dye attaining the saturation within 30 minutes and for Congo red, within 40 minutes. It is also found that % age adsorption of Congo red dye is more on Lady Finger stem as compared to Sunset Yellow dye. There is increase in adsorption of dyes by Lady Finger stem steadily in the beginning of process and then become slow and stagnate with the passage of time after optimized condition of contact interval because all available locations on the surface of adsorbent were covered and no active site available for further binding of dye molecules[18, 19].

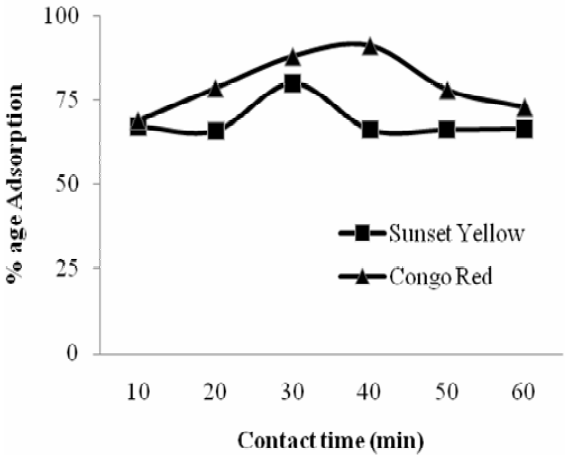

Fig. 3: Effect of contact time of Lady Finger stem with aqueous solution of dye on % age removal of Congo Red and Sunset yellow from water.

Table-1: Characteristic vibrational frequencies of *Abelmoschus esculentus* stem FT-IR spectrum.

Vibrational Assignment	Wave number (cm^{-1})
O-H	Broad band in 3600–3100 range
C-H stretching vibration from CH and CH_2	2920, 2852
C=O stretching vibration	1739
C=C stretching of aromatic ring	1517
CH_2 symmetric bending	1432
C-O stretching vibration of the acetyl group	1381, 1245
C-H and C-O of aromatic ring (bending vibration)	1368, 1322
anti-symmetrical deformation of the C-O-C	1156
C-O and O-H (stretching vibration)	1035
β -glycosidic linkage	894

2. Effect of Dye Solution pH

The pH of the dye solution plays a dominating role in adsorption processes, because it controls the magnitude of electrostatic charges which are imparted by the ionized form of dye molecules in aqueous media [1]. Using Lady Finger stem, the effect of pH on adsorption of Sunset Yellow and Congo Red dyes was studied and results are shown in Fig. 4, which reveals that the maximum adsorption of Sunset yellow was obtained at pH 5.0 and for Congo Red at pH 8.0. The maximum % age removal of Sunset yellow dye was 97.63 % and for Congo Red dye, it was 96.48 %. Anionic dyes are first dissolved in water and then their sulfonate groups are dissociated, converting them into anionic form, which usually aggregated. This aggregation helps in the proficient removal of these dyes by chemisorption on adsorbents, containing lingo-cellulosic materials which are usually of agro-waste origin [10, 12, 16].

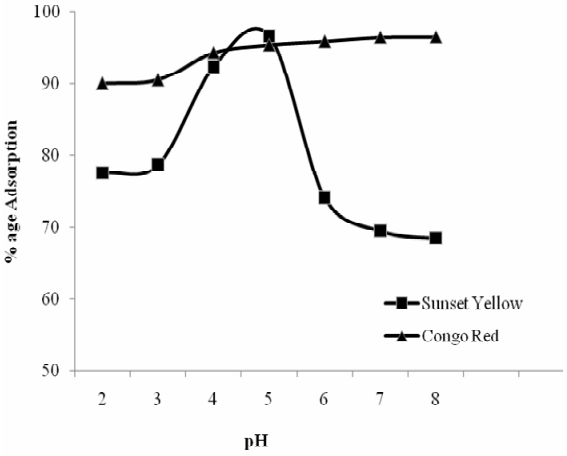

Fig.4: Effect of initial pH of dye solution using Lady Finger stem on % age removal of Congo red and Sunset yellow from water.

3. Effect of Adsorbent Dose

Adsorbent dosage effect on adsorption of Congo Red and Sunset Yellow dyes by Lady Finger stem was investigated and results are presented in Fig. 5. It is observed that maximum removal of Congo Red dye occurred with adsorbent dose of 0.5 g and in case of Sunset Yellow, 2.5 g adsorbent dose gives maximum adsorption. Low adsorbent dosage requirements depicted that Lady Finger stem had more binding sites available for adsorption of dyes in short interval of time. After optimized conditions of adsorbent dose, adsorption rates gradually decreases in case of Congo Red dye.

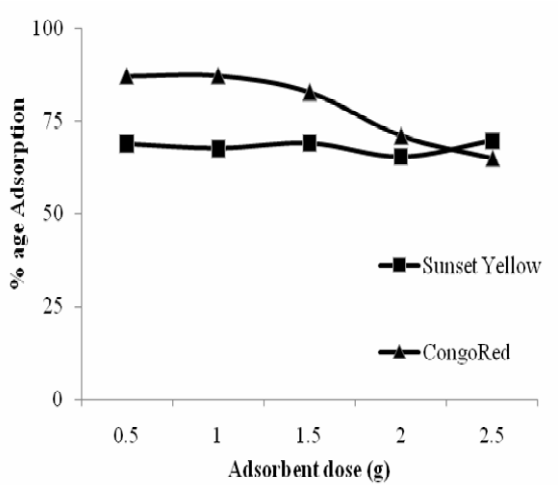

Fig. 5: Effect of adsorbent dose of Lady Finger stem % age removal of Congo Red and Sunset yellow dye from water.

4. Effect of Particle Size

Particle size of adsorbent is related with the surface area exposed to the adsorbate [16, 25]. Different mesh sized Lady Finger stem particles were used for adsorption of Congo Red and Sunset Yellow dyes and results are given in Fig. 6.

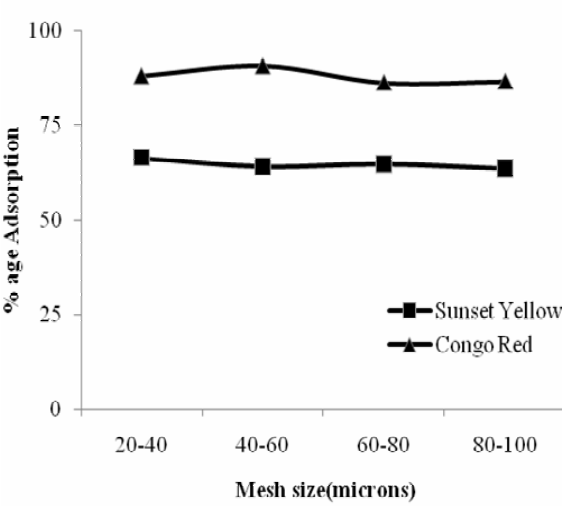

Fig. 6: Effect of particle size of Lady Finger stem % age removal Congo Red and Sunset yellow dye from water.

Mesh size is inversely related with the surface area of the adsorbent. As pore size in mesh increases, particle size decreases, resulting in more fine powder which can interact with adsorbate more efficiently. Maximum adsorption of Congo Red dye

is observed at 40-60 microns sized Lady Finger stem particles and for Sunset yellow at 20-40 microns as clear from Fig. 6.

5. Effect of Agitation Rate

Agitation of dye solution facilitates better interaction between adsorbate species and external surface of adsorbent particles and prevents agglomeration of adsorbent particles, but if the agitation speed exceeds from limits, it hinders in adsorption process. So, agitation speed conditions were optimized for adsorption of Congo Red and Sunset Yellow dyes by Lady Finger stem and results are shown in Fig. 7. For Congo red, maximum adsorption was observed at an agitation rate of 150 rpm and for sunset yellow at 50 rpm. Further increase in agitation speed after optimized conditions did not improve adsorption in both cases.

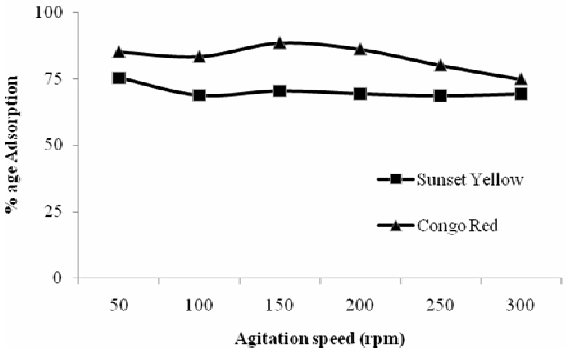

Fig.7: Effect of agitation rate on % age removal of Congo Red and Sunset yellow from water using Lady Finger stem.

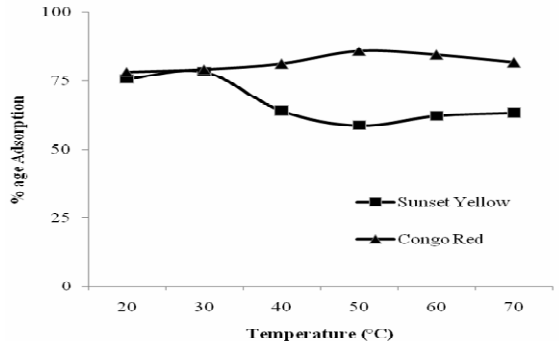

Fig. 8: Effect of temperature on % age removal of Congo Red and Sunset yellow dye from water using Lady Finger stem.

6. Effect of Temperature

The effect of dye solution temperature on adsorption process was investigated and shown in Fig. 8. The maximum adsorption value for Sunset yellow and Congo Red dyes was obtained when the temperature was 30 and 50^0C respectively. Increasing temperature further results in a decrease in adsorption, because adsorption is an exothermic process. High temperature conditions also initiate thermal degradation of dye species and cellulosic type adsorbents, so it is usually avoided.

Isothermal Investigation of Equilibrium Data

1. Langmuir Modeling

The Langmuir model is used to describe the adsorptive behaviour of homogeneous surfaces by monolayer chemisorption, with no sideways interaction between adsorbate species with different layers of adsorbent surfaces. Table-2 is showing Langmuir isothermal parameters for Congo Red and Sunset Yellow dyes adsorption by Lady Finger stem. The correlation coefficient 'R^2' values in Langmuir model are 0.943 and 0.972 for Congo Red and Sunset Yellow dyes respectively, depicting this model on equilibrium data. Maximum adsorption capacity of Lady Finger stem 'q_m' was 24.59 and 15.92 mg/g for Congo Red and Sunset Yellow dyes respectively.

Whereas other Langmuir parameter 'b' is used to calculate separation factor 'R_L' and thermodynamic parameter 'ΔG^{o}'. Separation factor is used to determine favorable or unfavorable nature of adsorption system. If R_L value is less than one, then adsorption is favorable and vice versa, whereas zero R_L value means adsorption process is irreversible and R_L=1 means adsorption is linear [21-24]. Its value for Congo Red and Sunset Yellow dyes was 0.87 and 0.91 respectively, means adsorption of these dyes was favorable with Lady Finger stem. Negative values of ΔG^{o} predict the feasibility of this adsorption process at larger scale, as it is on batch scale [25]. It shows that Lady Finger stem can also be used at larger scale for dye adsorptive removal processes.

Table-2: Langmuir and thermodynamical modeling of equilibrium data for adsorption of Congo Red and Sunset Yellow by Lady Finger stem.

	Langmuir Isotherm Parameters					Separation Factor R_L	Thermodynamical Parameters
Dye	Slope	Intercept	R^2	q_m(mg/g)	b (L/g)		ΔG^o(kJ/mol)
Congo Red	12.484	0.041	0.943	24.59	0.003	0.87	-14.39
Sunset Yellow	29.381	0.063	0.972	15.92	0.002	0.91	-15.40

2. Freundlich Modeling

This model is applicable in those conditions, where adsorbent has heterogeneous nature and multi-layer physiosorption occurred during removal of adsorbate species. Table-3 is showing Freundlich isothermal parameters for Congo Red and Sunset Yellow dyes adsorption by Lady Finger stem. 'K_F' values were 0.12 and 0.04 $mg^{1-1/n}\ L^{1/n}\ g^{-1}$ for Congo Red and Sunset Yellow dyes respectively. The other Freundlich parameter '*n*' values less than 8 show the feasibility of the process at lower dye concentration. It is basically denoting adsorption intensity, which gradually varies with heterogeneity of surface of adsorbent [13, 14]. Its values for Congo Red and Sunset Yellow dyes 1.183 and 1.119 respectively using Lady Finger stem as adsorbent.

Table-3: Freundlich modeling of equilibrium data for adsorption of Congo Red and Sunset Yellow by Lady Finger stem.

Dye	Freundlich Isotherm Parameters				
	Slope	Intercept	R^2	$K_F(mg^{1-1/n}\ L^{1/n}\ g^{-1})$	n
Congo Red	0.845	-0.921	0.951	0.12	1.183
Sunset Yellow	0.893	-1.347	0.978	0.04	1.119

3. Temkin Modeling

Table-4 is showing Temkin isothermal parameters for adsorption of Congo Red and Sunset Yellow dyes by *Abelmoschus esculentus* stem. Equilibrium binding constant 'K_T' values for Congo Red and Sunset Yellow dyes were 0.16 and 0.15 L/mg. Heat of adsorption 'B_T' was 1.381 and 0.650 for Congo Red and Sunset Yellow dyes respectively. Its values less than 8 are an indication of physiosorption of anionic dyes by Lady Finger stem [29].

Table-4: Temkin modeling of equilibrium data for adsorption of Congo Red and Sunset Yellow by Lady Finger stem.

Dye	Temkin Isotherm Parameters				
	Slope	Intercept	R^2	K_T(L/mg)	B_T(kJ/mol)
Congo Red	1.381	-2.505	0.985	0.16	1.381
Sunset Yellow	0.650	-1.237	0.988	0.15	0.650

Experimental

Chemicals and Instrumentation

Analytical grade chemicals were used in this work as received without any further processing. Sunset Yellow dye (M.W: 452.36 g/mol, λmax: 482nm, Fluka), Congo Red dye (M.W: 696.66 g/mol, λmax: 500 nm, Fluka), HCl (Merck), NaOH (Merck). Electric Balance ER-120A (AND), Electric grinder (Ken-Wood), pH meter (HANNA pH 211), UV-Vis Double Beam spectrophotometer (Spectro UVD-3500, Labomed), FT-IR spectrometer (Perkin Elmer-RX) were used for processing and analysis.

Preparation of Adsorbent and Synthetic Dye Wastewater Preparation

Stem of Lady Finger was collected from different rural areas of District Gujrat, Pakistan. All of them were repeatedly washed with water and dried in sunlight for 8-12 days. After drying, they were subjected to crushing and grinding into fine powder. They were dried in oven at 80ºC for complete removal of moisture and stored in air tight plastic jars till further use.

Stock solutions of dyes of 1000 mg/L concentration were prepared by dissolving their 0.1 g/100 mL in distilled water. Working solutions and standards were prepared by further dilutions of stock solutions.

Adsorption Experiments

Various factors effecting adsorption capacity of Lady Finger stem for removing anionic dyes were optimized by varying them one by one, keeping the other constant using both dyes solutions separately by following same methodology as described earlier [25]. The % age removal of dye at any instant of time was determined by equation 1:

$$\%\text{ age adsorption} = \frac{C_o - C_e}{C_o} \times 100 \qquad (1)$$

Isothermal and Thermodynamical Studies

For describing the description mechanism of adsorption, isothermal and thermodynamical studies were carried out by employing all the optimized conditions of all operating parameters on higher concentration of dye solutions, i.e. 30-80 mg/L with the difference of 10. Adsorption capacity of adsorbent at any instant 'q' is calculated by equation-2:

$$q = \frac{(C_o - C_e)V}{m} \qquad (2)$$

Three isothermal models were used for determining mechanism of adsorption namely: Langmuir, Freundlich and Temkin models. Their straight line linear plots can be drawn by employing equation 4-6 were given [25-30].

$$\frac{1}{q} = \frac{1}{bq_m C_e} + \frac{1}{q_m} \quad (3)$$

$$\log q = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

$$q = B_T \ln C_e + B_T \ln K_T \quad (5)$$

Langmuir Separation factor 'R_L' was calculated with equation-6:

$$R_L = \frac{1}{(1_o + bC_o)} \quad (6)$$

In these equations, C_o and C_e are the initial and final concentrations of dye respectively, 'q' (mg/g) is the amount of dye removed by biosorbent, 'q_m' (mg/g) and b (L/g) are Langmuir isotherm parameters. In equation-4, 'K_F' ($mg^{1-1/n}\ L^{1/n}\ g^{-1}$) and 'n' (L/mg) are Freundlich isotherm constants. Whereas in equation-5, 'B_T' (KJ/mol) and 'K_T' are Temkin isotherm constants. All the constants were determined by the regression analysis of linear plots of respective isotherms. For calculating 'ΔG^o' equation-7 was used:

$$\Delta G^o = -RT \ln K \quad (7)$$

Here 'ΔG^o' is in KJ/mol, *'R'* is the universal gas constant, *'T'* is the absolute temperature in Kelvin and '*K'* is the reciprocal of Langmuir constant '*b*' [25].

Conclusion

It can be safely concluded from this study that Lady Finger stem can remove Congo Red and Sunset Yellow from water efficiently. Maximum adsorption capacity for Congo Red and Sunset Yellow dyes were 24.59 and 15.92 mg/g respectively. The feasibility of adsorption system was supported by separation factor 'R_L', adsorption intensity '*n*' and thermodynamic parameter 'ΔG^o'. These results suggested that Lady Finger stem can be used on larger scale for dyes removal from waste water by adsorption methodology.

References

1. M. A. M. Salleh, D. K. Mahmoud, W. A. W. A. Karim and A. Idris, *Desalination*, **280**, 1(2011).
2. A. Demirbas, *Journal of Hazardous Materials*, **167**, 1 (2009).
3. Y. Yang, G. Wang, B. Wang, Z. Li, X. Jia, Q. Zhou and Y. Zhao, *Bioresource Technology*,**102**, 828 (2011).
4. A. Mittal, J. Mittal, A. Malviya and V. K. Gupta, *Journal of Colloid and Interface Science*, **340**, 16 (2009).
5. C. Pelekania and V. L. Snoeyink, *Carbon*, **39**, 25 (2001).
6. J. Huff, *Environmental Health Perspectives*, **45**, 209 (1982).
7. O. D. Olukanni, A. A. Osuntoki, G. O. Gbenle, *African Journal of Biotechnology*, **5**, 1980 (2006).
8. R. Jain and S. Sikarwar, *International Journal of Environment and Pollution*, **27**, 158 (2006).
9. M. M. Ghoneim, H. S. El-Desoky and N. M. Zidan, *Desalination*, **274**, 22 (2011).
10. I. D. Mall, V. C. Srivastava, N. K. Agarwal and I. M. Mishra, *Chemosphere*, **61**, 492 (2005).
11. C. Namasivayam, N. Muniasamy, K. Gayatri, M. Rani and K. Ranganathan, *Bioresource Technology*, **57**, 37 (1996).
12. C. Namasivayam, C. D. Prabha and M. Kumutha, *Bioresource Technology*, **64**, 77 (1998).
13. G. McKay, G. Ramprasad and P.P. Mowli, *Water*, *Air and Soil Pollution*, **29**, 273 (1986).
14. K.G. Bhattacharya and A. Sharma, *Dyes and Pigments*, **65**, 51 (2005).
15. P. Waranusantigul, P. Pokethitiyook, M. Kruatrachue and E. S. Upatham, *Environmental Pollution*, **125**, 385 (2003).
16. D. N. Jadhav and A. K. Vanjara, *Indian Journal of Chemical Technology*, **11**, 35 (2004).
17. V.K. Gupta, A. Mittal, L. Krishnan and V. Gajbe, *Separation and Purification Technology*, **40**, 87 (2004).
18. V. K. Gupta, D. Mohan, S. Sharma and M. Sharma, *Separation Science and Technology*, **35**, 2097 (2000).
19. A. Mittal, L. Krishnan and V. K. Gupta, *Separation Science and Technology*, **43**, 125 (2005).
20. V. K. C. Grag, M. Amita, R. Kumar and R. Gupta, *Dyes and Pigments*, **63**, 243 (2004).
21. R. Gong, Y. Sun, J. Chen, H. Liu and C. Yang, *Dyes and Pigments*, **67**, 175 (2005).
22. G. Moussavi and R. Khosravi, *Chemical Engineering Research and Design*, **89**, 2182 (2011).
23. N.K. Amin, *Journal of Hazardous Materials*, **165**, 52 (2009).
24. G. Moussavi and R. Khosravi, *Chemical Engineering Research and Design*, **89**, 2182 (2011).
25. R. Rehman, J. Anwar and T. Mahmud, *Journal of the Chemical Society of Pakistan*, **34**, 460 (2012).

26. M. Duldulao, H. Watanabe, Y. Kamaya and K. Suzuki, *Wood Industry*, **65**, 256 (2010).
27. M.S. Alam and G.M. A. Khan, *Journal of Textile and Apparal*, *Technology and Management*, **5**, **1** (2007).
28. I. M. De Rosa, J. M. Kenny, M. Maniruzzaman, M. Moniruzzaman, M. Monti, D. Puglia, C. Santulli and F. Sarasini, *Composites Science and Technology*, **71**, 246 (2011).