REMOVAL OF RHODAMINE-B FROM AQUEOUS SOLUTIONS USING LOW COST ADSORBENTS

NIKITA CHOUDHARY, SANWAL RAM, ASHVINI SHARMA, SHOBHA SHARMA and VIMLA CHOWDHARY[*]

Department of Chemistry, J. N. V. University, JODHPUR – 342005 (Raj.) INDIA

ABSTRACT

Colored wastewater damages the esthetic nature of water and the photosynthetic activity of aquatic organisms. Dyes are widely used as coloring agents in various industries, such as plastics, textile, and paper & pulp industry. In the present study, 1:1 ratio mixture of some low cost materials like activated carbon and fly ash mixtures were used for the adsorption of Rhodamine-B. Batch method was employed for this study to explore the feasibility of using activated carbon and fly ash mixture as a low-cost biosorbent for the removal of Rhodamine-B from aqueous solutions. The effect of physico-chemical variables such as dose level, solution pH, initial dye concentration, contact time, and temperature was also investigated. Both the isotherms, Langmuir and Freundlich models exhibited excellent fit to the equilibrium biosorption data. The maximum monolayer biosorption capacity of 82.6 was attained at optimum pH (6.0), adsorbent dose (5 g), initial dye concentration (50 ppm), temperature (35ºC), and contact time (150 min), which was higher than those of many other sorbent materials.

Key words: Batch experiments, Freundlich isotherm, Langmuir isotherm, Rhodamine-B.

INTRODUCTION

The huge rate in population growth has increased the demand for industrial products. Natural and synthetic dyes, as one of the main groups of organic pollutants, are extensively used in several industries like textile, paper and pulp, leather, plastics, dyeing and printing. These products so generated lead to the formation of wastewater contaminated with dyes. Typical textile effluents contain various types of dye molecules[1]. Most of dyes are non-biodegradable and stable, having carcinogenic action[2], due to their synthetic nature and aromatic character.

Color removal from textile effluents has been the target of great concern of chemists

_____

[*]Author for correspondence; E-mail: dr.vimlachoudhary@gmail.com

in the last few years, not only because of its potential toxicity, but mainly due to its visibility problems also[3-4]. The conventional treatment methods for dye effluents, such as oxidation[5-6], coagulation[7-8], flocculation[9], photochemical destruction[10], ion exchange and membrane filtration[11], are complicated and costly, in particular as some methods require additional chemicals or produce toxic products[12]. Among these methods, adsorption has been shown to be one of the alternatives for the removing of dyes from aqueous solutions[13,14].

The major advantages of adsorption system for water pollution control are good removal performance, less investment in terms of initial cost, flexibility, simplicity of design, easiness of operation and insensitivity to toxic pollutants as compared to the conventional biological treatment[15,16]. Therefore, in the recent past, there has been an increasing interest to find cheaper and easily provided natural adsorbents, which are compatible with the environment. Certain natural resources such as banana pith[17], rice husk[18], papaya seeds[19], orange peel[20], waste cotton[21], bentonite clay[22], neem leaf powder[23], palm shell[24] bamboo dust, coconut shell and groundnut shell[25], duck weed[26], sewage sludge[27], Caulerpalentillifera[28], Posidoniaoceanica[29], Camel thorn plant[30], Chamomilla plant[31], minerals[32] and fly ash[33,34] have already been used by previous workers.

In the present study, we report the use of low cost natural environmental waste adsorbent i.e. activated carbon and fly ash mixture in a ratio of 1:1 for the removal of Rhodamine-B dye from aqueous solution that is economically viable, easily available and more effective. Batch method has been employed to obtain the better understanding of bio-sorption mechanism of dye removal. The effect of biosorption process variables such as dose, solution pH, initial dye concentration, contact time, temperature have also been investigated on dye removal efficiency. Due to wide range of industrial use, Rhodamine-B was selected for this study as an azo-based dye model.

EXPERIMENTAL

Materials

Chemicals used are of AR grade and double distilled water is used in all studies.

Standard dye solution

Rhodamine-B ($C_{28}H_{31}ClN_2O_3$) ([9-(2-carboxyphenyl)-6-diethylamino-3-xanthenyli-dene]-diethylammonium chloride) (RB) was used as the adsorbate in this study (Fig. 1). The dye solutions used in the experiments (1000 mg/L) were prepared by dissolving the required amount of dye in double distilled water. The working solutions were prepared by diluting the stock solution. The RB concentration was determined by measuring the absorbance at

λ_{max} 543 nm against a standard curve (Fig. 2). The concentration of the residual dye was measured using UV/visible spectrometer at a wavelength corresponding to the maximum absorption for the dye solution (λ_{max} = 543 nm) by withdrawing samples at fixed time intervals, which was filtered, and the supernatant was analysed for residual RB.
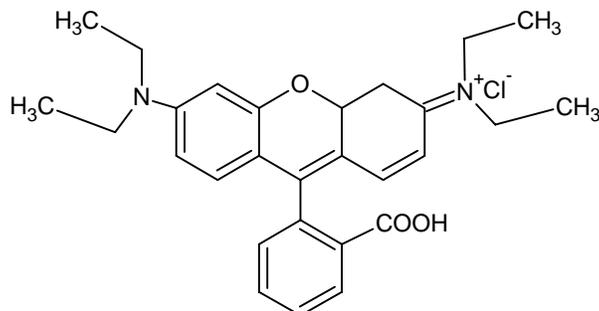
Fig. 1: Structure of rhodamine-B
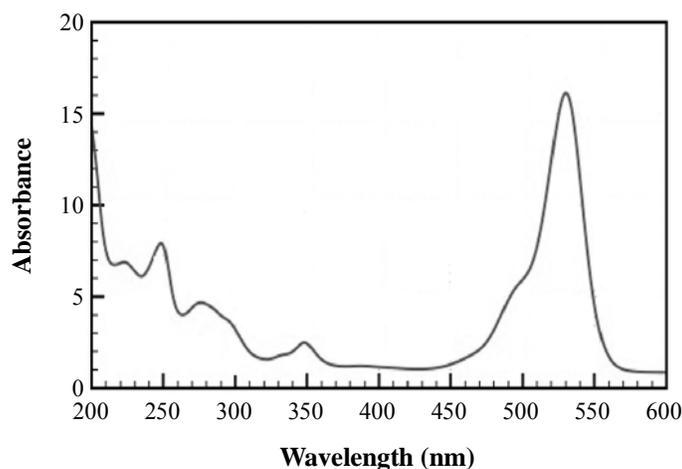
Fig. 2: UV-Vis spectrum of rhodamine-B

Adsorbent preparation

Preparation of activated carbon (AC)

The coconut shell pieces were washed repeatedly with distilled water for removing dust, dried in an oven at 100ºC and subsequently soaked in phosphoric acid (H_3PO_4) solution for one day for protonation of biomass. Then, the adsorbent was filtered and heated till dryness. In the next step, the adsorbent was carbonized at 220ºC for 18 hrs. The activated product was then cooled to room temperature. Finally, this carbonized material was

grounded and sieved to obtain desired size (250 μ) carbon particle and used as chemically activated adsorbent and stored in an air-tight polyethylene bottles.

Procurement and preparation of fly ash as adsorbent

Fly ash (FA) (derived out of the bituminous coal) was obtained from Faridabad Thermal Power Plant, Haryana. The sample received was washed with distilled water to remove surface dust and was dried in oven at 110ºC for 1 hr. Fly ash samples were stored in airtight polyethylene containers. The major components of this FA are alumina, silica, iron oxide, calcium oxide and residual carbon.

Preparation of adsorbent

The ability of AC-FA mixture for removal of colour from industrial effluent was investigated. Activated carbon prepared from coconut shell with fly ash mixture in 1:1 ratio was used for effluent treatment study as adsorbent dose.

Batch adsorption experiment

To evaluate the efficiency of adsorbents, batch adsorption experiments were carried out. In each adsorption experiment, 100 mL of dye solution of known concentration and pH was added to 1.0 g of adsorbents in 250 mL round bottom flask at room temperature (35ºC) and the mixture were stirred on a teflon stirrer in milestone microwave solvent extractor system (ETHOS SEL) at 200 rpm. The initial pH of the mixture varied between 4-10. This was controlled by the addition of dilute hydrochloric acid or sodium hydroxide solution. At the end of pre-determined time intervals, mixed adsorbent was removed from dye solution by vacuum filtration through 0.45 μm nylon filter membrane. The filtrate was analyzed spectrophotometrically for residual concentration of dyes at 543 nm. The experiments were carried by varying the amount of adsorbents (1.0 to 7.0 g 100 mL^{-1}), concentration of dye solution (50-250 mg L^{-1}) and pH (2 to 8) at different time intervals (30-210 min). The adsorbed amount was determined by the following formula:

$$q_e = \frac{V(C_o - C_e)}{m} \qquad \qquad \ldots(1)$$

where q_e is the amount of adsorbed solute per weight of adsorbent at equilibrium, V is the solution volume, m is the mass of activated carbon, C_o and C_e are the initial and equilibrium concentration of adsorbate, respectively.

The data so obtained by adsorption batch experiments were fitted in Langmuir and Freundlich isotherm models.

RESULTS AND DISCUSSION

Effect of pH

The effect of pH on dyes RB by AC-FA mixture from 5 g L^{-1} solute in 150 min. at temperature 35ºC is shown in Table 1 and Fig. 3 (The initial dye concentration = 50 ppm, adsorbent dose = 5 g L^{-1}, contact time = 150 min, solution temp. = 35ºC and agitation speed = 200 rpm).

Table 1: Effect of pH on percent removal of dyes (Initial concentration 50 ppm)

pH	4	5	6	7	8	9	10
% Removal	88.2	90.3	92.2	91.0	90.1	89.6	85.5
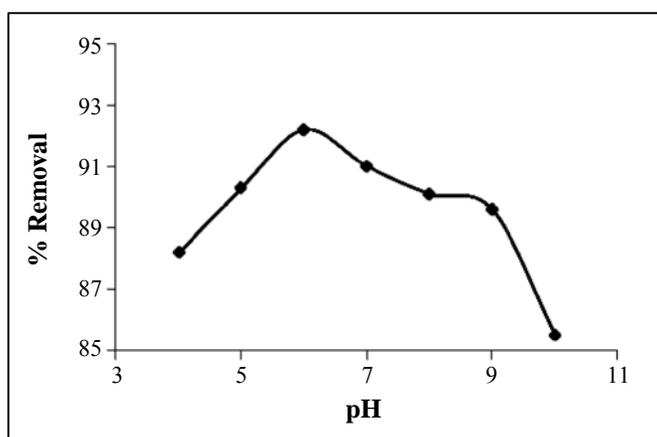
Fig. 3: Effect of the pH on the adsorption of RB dye onto AC-FA

The H^+ ion concentration (pH) primarily affects the degree of ionization of the dyes and the surface properties of absorbent. (Fig. 3). It is clear that the amount of dye removed varies with pH i.e. the maximum absorption was found at pH 6. Above and below this pH, adsorption of dyes on adsorbent tends to decrease slightly[35]. This can be explained on the basis of formation of positively charged surface on adsorbent due to neutralization of negatively charged adsorbent surface; thereby, reducing hindrance of the diffusion of dyes at acidic pH.
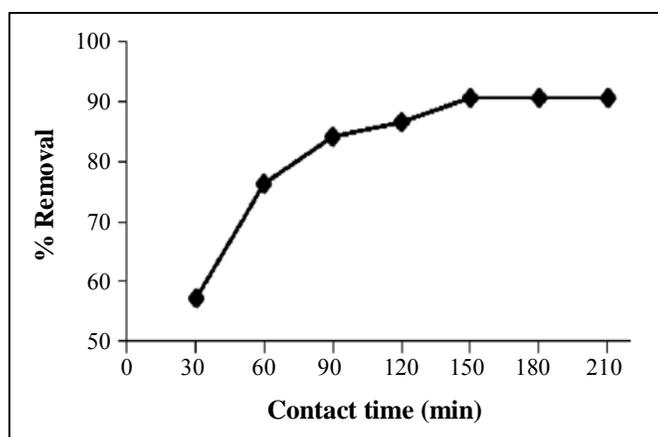
Effect of contact time

The effect of contact time on the amount of dye adsorbed was investigated at 50 ppm concentration of the dye at pH 6. It is observed that the percentage removal of dye increases

rapidly with an increase in contact time initially, and thereafter, beyond a contact time of about 180 min, no noticeable change in the percentage removal is observed Fig. 4; (dye concentration = 50 ppm, adsorbent dose = 5 g L^{-1}, solution temp. = 35ºC and agitation speed = 200 rpm). The percentage removal after 180 min were constant i.e. 90.6%. Therefore, the optimum contact time is considered to be 180 min. This is also the equilibrium time of the batch adsorption experiments, since beyond a contact time of 180 min, adsorption is not changed. The rapid removal of dye is observed at the beginning of the contact time due to the percentage of large number of binding sites available for adsorption[36]. The smooth and independent nature of curve indicates formation of monolayer cover of the dye on the outer surface of adsorbent. The experimental results of adsorptions of RB by AC-FA mixture is shown in Table 2.

Table 2: Effect of contact time on percentage dye removal

Contact time (min)	30	60	90	120	150	180	210
% Removal	57.2	76.2	84.2	86.5	90.6	90.6	90.6

**Fig. 4: Effect of contact time on the adsorption of RB dye onto AC-FA**

Effect of adsorbent dose

The effect of adsorbent dosage (1-7 g) was investigated on the adsorption of RB and the results are represented in Table 3. As can be seen in Fig. 5 (initial dye concentration = 50 ppm, adsorbent dose = 5 g L^{-1}, contact time = 150 min, solution temp. = 35ºC and agitation speed = 200 rpm), dye removal efficiency increased rapidly with increasing adsorbent until it reached the value of 92.6% having the adsorbent content of 5 g. The increase in removal

rate of RB can be explained by the increased surface area of the adsorbent and availability of more binding sites for dye molecules[37]. On the other hand, further increase in the adsorbent dosage beyond 5 did not significantly change the adsorption yield. This was due to the binding of almost all dye ions to adsorbent surface and the maintenance of equilibrium between the dye molecules on the adsorbent and those present in the solution[38].

Table 3: Effect of AC-FA mixture dose on percentage dye removal

Adsorbent dose (g L^{-1})	1	2	3	4	5	6	7
% Removal	28.9	49.2	66.4	78.6	92.6	92.0	92.1
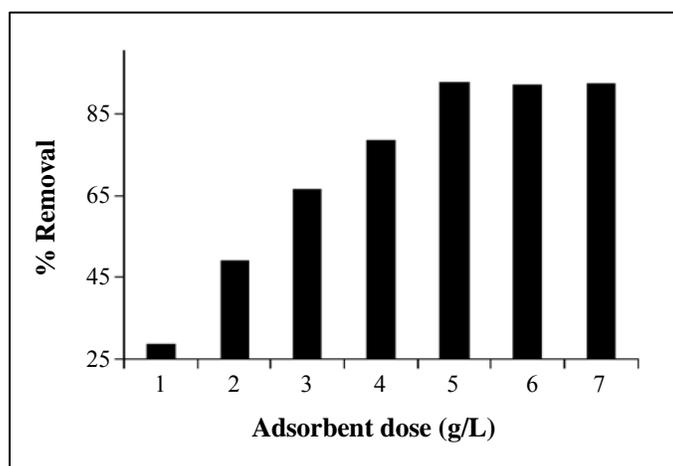
**Fig. 5: Effect of AC-FA mixture dose on adsorption of RB dye onto AC-FA**

Effect of initial dye concentration

The effect of initial dye concentration onthe percentage removal of Rhodamine-B (50, 100, 150, 200 and 250 mg L^{-1}) has been shown in Fig. 6 (initial dye concentration = 50 ppm, adsorbent dose = 5 g L^{-1}, contact time = 150 min, solution temp. = 35ºC and agitation speed = 200 rpm). It was observed that the percentage removal of dye decreases with the increase in the concentration of dye solution (Table 4). This is because at lower concentration, the ratio of dye to the available surface area is low. Subsequently, the adsorption is high. However, at high concentration, the available sites of adsorption becomes

fewer and hence, the percentage removal of dye is less. Similar results are reported in literature[39].

Table 4: Effect of initial dye concentration on percentage dye removal

| Initial dye concentration (ppm)	50	100	150	200	250
% Removal	91.5	85.8	82.6	71.4	56.3
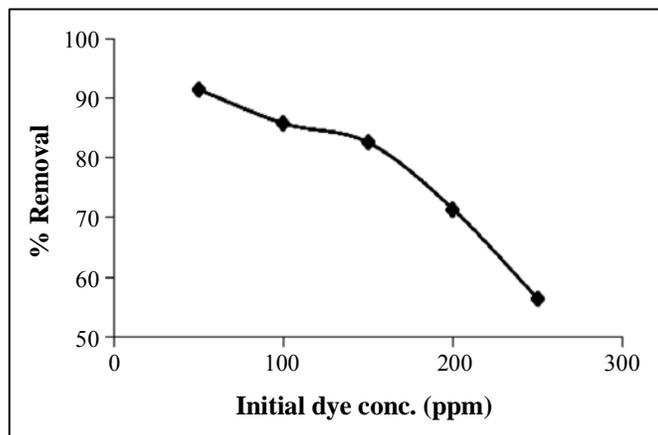
Fig. 6: Effect of initial dye concentration adsorption of RB onto AC-FA

Effect of temperature

It was determined at three different temperatures (25°, 35° and 45°C) in equilibrium condition (Table 5). Thermodynamic parameter like heat of absorption and energy of activation play an important role in predicting the absorption behavior as both are strongly dependent on temperature. The percentage dye removal, increased with increase temperature (25° to 45°C) with 5 g L^{-1} in 150 min for 50 ppm dye solution is shown in Fig. 7 (initial dye concentration = 50 ppm, adsorbent dose = 5 g L^{-1}, contact time = 150 min, solution temp. = 35ºC and agitation speed = 200 rpm). This behavior was due to the possibility of an increase in the porosity and total pore volume of the adsorbent with the temperature.

Table 5: Effect of temperature on percentage dye removal

Temperature (°C)	25	35	45
% Removal	84.2	91.2	91.5
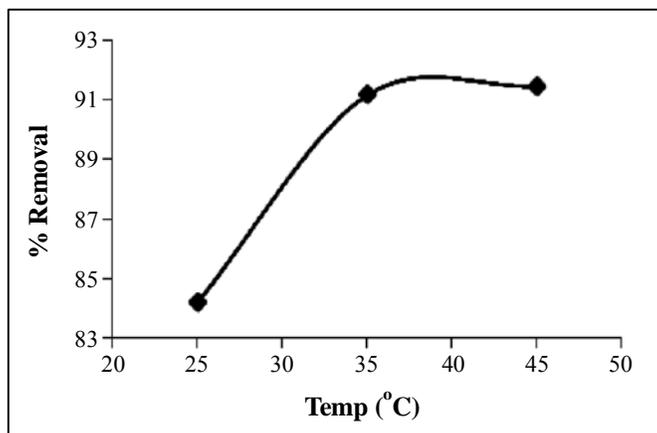
Fig. 7: Effect of temperature on adsorption of RB dye onto AC-FA

Adsorption isotherm

Equilibrium data, commonly known as adsorption[40] isotherms, are basic requirements for the design of adsorption systems[41]. In the present work, Langmuir, and Freundlich models were employed for the equilibrium data of RB on AC-FA. The linear plot of specific adsorption (C_e/q_e) against the equilibrium concentration (C_e) (Fig. 8) shows that the adsorption obeys the Langmuir model. The Langmuir constants q_m and K_a were determined from the slope and intercept of the plot and are presented in Table 6. The value of the correlation coefficient ($R^2 = 0.979$) obtained from Langmuir expression indicates that Langmuir expression provided a good linearity. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given by the following equation[42]:

$$R_L = 1/ (1+ K_a C_o) \qquad \qquad …(2)$$

where C_0 (mg L^{-1}) is the initial concentration of adsorbate, and K_a (L mg^{-1}) is Langmuir constant. The value of R_L indicates the shape of the isotherm, which is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). The R_L values for the adsorption of RB onto AC-FA are observed to be in the range 0–1, indicating that the adsorption was a favorable process (Table 6).

The equilibrium data were further analyzed using the linear form of Freundlich isotherm, by plotting log q_e versus log C_e (Fig. 9). The calculated Freundlich isotherm constants (K_F, n) and the corresponding coefficient of correlation, R^2 are shown in Table 6. The coefficient of correlation is $R^2 = 0.871$, which is expressing an agreement with the 87%

of experimental data of RB on AC-FA. The result shows that the value of 1/n is lying in the range of 0-1 (n = 0.189) indicating that the dye is favorably adsorbed on AC-FA. This is in good agreement with the findings regarding to R_L value. The magnitude of Freundlich constant indicates easy uptake of RB from aqueous solution.

Table 6: Isotherms parameters for removal of RB on AC-FA

Isotherm	Langmuir constant				Freundlich constant			
Parameters	a	b	R^2	R_L	Intercept	K	1/n	R^2
Value	14.92	0.174	0.979	0.174	0.819	6.58	0.189	0.871
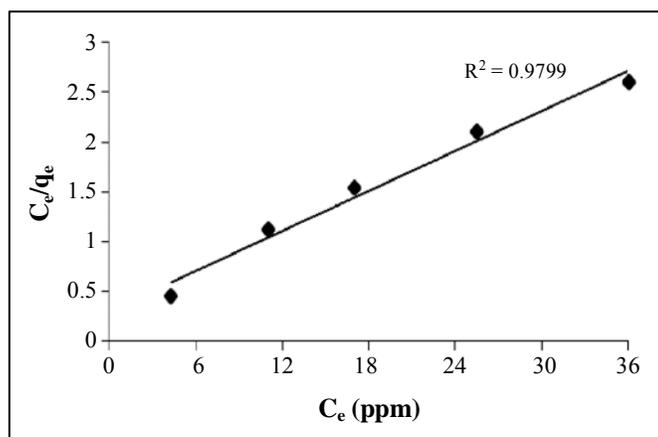
Fig. 8: Langmuir isotherm plot for adsorption of RB dye onto AC-FA
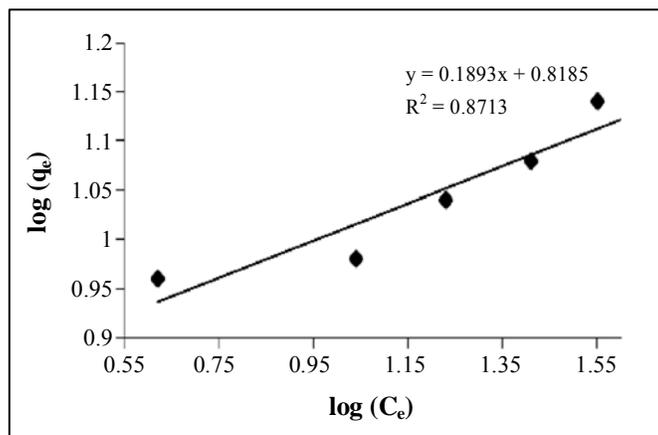
Fig. 9: Freundlich isotherm plot for adsorption of RB dye onto AC-FA

CONCLUSION

It is concluded from the above results and discussion that adsorbent mixture (AC-FA 1:1 mixture) showed best adsorption capacity at pH 6, contact time 150 min, temperature 35°C, and adsorbent dose 5 g L^{-1} for Rhodamine-B used in the present investigation. Equilibrium adsorption data were well described by the Langmuir and Freundlich adsorption isotherm models. The higher values of K indicate higher adsorption capacity of adsorbent and the value of 1/n is ranging from 0 to 1, shows favorable adsorption. 1:1 mixture of activated carbon-fly ash is effective in adsorption capacities of azo dyes from aqueous solution and textile wastes.

ACKNOWLEDGEMENT

REFERENCES

1. C. Phalakornkule, S. Polgumhang, W. Tongdaung, B. Karakat and T. Nuyut, J. Environ. Man., **91(4)**, 918 (2009).

2. G. Crini, Bioresour. Technol., **97**, 1061 (2006).

3. R. Yu-Li Yeh and A. Thomas, J. Chem. Tech. Biotechnol., **63**, 55 (1995).

4. L. Morais, O. Freitas, E. Gancolves, L. Vaskancelos and C. Gonzalez, Water Res., **33**, 979 (1999).

5. I. Arslan, I. A. Balcioglu and D. W. Bahnemann, Dyes Pigments, **47**, 207 (2000).

6. K. S. Thangamani, M. Sathishkumar, Y. Sameena, N. Vennilamani, K. Kadirvelu, Turgaya, G. Ersoza, S. Atalaya, J. Forssb and U. Welanderb, Sep. Puri. Tech., **79**, 26 (2011).

7. A. Szygu, E. Guibal, M. A. Palacín, M. Ruiz and A. M. Sastre, J. Environ. Manag., **90**, 2979 (2009).

8. A. K. Verma, D. R. Roshan and P. Bhunia, J. Environ. Manag., **93**, 154 (2012).

9. Y. Wang, B. Gao, Q. Yue, Y. Wang and Z. Yang, Biores. Tech., **113**, 265 (2012).

10. N. Deng, F. Wu, F. Luo and Z. Liu, Chemosphere, **35**, 2697 (1997).

11. G. Ciardelli, L. Corsi and M. Marucci, Res., Cons. Recy., **31**, 189 (2000).

12. L. Wang and J. Li, Indus, Crops Products, **42**, 153 (2013).

13. T. Madrakian, A. Afkhami and M. Ahmadi, Mol. Biomol. Spect., **99**, 102 (2012).

14. K. Kadivelu, M. Kavipriya, C. Karthika, M. Radhika, N. Vennilamani and S. Pattabhi, Biores. Tech., **87**, 129 (2003).

15. R. Ansari and Z. Mosayebzadeh, J. Iran. Chem. Soc., **7**, 339 (2010).

16. S. Schiewer and M. H. Wong, Chemosphere, **41(1)**, 271 (2000).

17. C. Namasivayam, D. Prabha and M. Kumutha, Biores. Tech., **64(1)**, 77 (1998).

18. U. R. New Lakshmi, V. C. Srivastava, I. D. Mall and D. H. Lataye, J. Environ. Manag., **90**, 710 (2009).

19. B. Hameed, J. Hazard. Mat., **162**, 939 (2009).

20. C. Namasivayam, N. Muniasamy, K. Gayatri, M. Rani and K. Ranganathan, Biores. Tech., **57 (1)**, 37(1996).

21. K. R. Ramakrishna and T. Viraraghavan, Water Sci. Tech., **36**, 189 (1997).

22. M. Dogan, M. Alkan, A. Turkyilmaz and Y. Ozdemir, Y., J. Hazard. Mater. B, **109**, 141 (2004).

23. G. M. Walker and L. R. Weatherley, Environ. Poll., **99**, 133 (1998) .

24. G. Sreelatha, V. Ageetha, J. Parmar and P. Padmaja, J. Chem. Eng. Data, **56**, 35 (2011).

25. N. Kannan and M. M. Sundaram, Dyes Pigments, **51**, 25 (2001).

26. M. Otero, F. Rozada, L. F. Calvo, A. I. Garcia and A. Moran, Biochem. Eng. J., **15**, 59 (2003).

27. F. Moghadasi, M. Momen Heravi, M. R. Bozorgmehr, P. Ardalan and T. Ardalan, Asian J. Chem., **22(7)**, 5093 (2003).

28. K. Marungrueng and P. Pavasant, Biores. Tech., **98**, 1567 (2007).

29. U. Dural, L. Cavas, F. Katsaros and S. Papageorgiou, Chem. Eng, J., **168(1)**, 77 (2011).

30. F. Moghadasi, M. M. Heravi, M. R. Bozorgmehr, P. Ardalan and T. Ardalan, Asian J. Chem., **22(7)**, 5093 (2010).

31. M. M. Heravi, A. Kodabande, M. R. Bozorgmehr, T. Ardalan and P. Ardalan, J. Chem. Health Risks., **4(2)**, 37 (2012).

32. C. C. Wang, L. C. Juang, T. C. Hsu, C. K. Lee, J. F. Lee and F. C. Huang, J. Colloid Interface Sci., **273**, 80 (2004).

33. K. D. Chaudhary, S. Sharma, S. Jain and V. Chowdhary, Int. J. Chem., **3(2)**, 218 (2014).

34. I. D. Mall, C. Srivastava and N. K. Agarwal, Dyes Pigments, **69**, 210 (2006).

35. V. K. Garg, M. Amita, R. Kumar and R. Gupta, Dyes Pigments, **63**, 243 (2004).

36. D. Aktas, S. N. Giray and Y. Uysal, J. S. U. Nat. App. Sci., 80 (2014).

37. T. Akar, I. Tosun, Z. Kaynak, E. Kavas, G. Incirkus and S. T. Akar, J. Hazard. Mater. **171(1)**, 867 (2009).

38. G. Akkaya and A. Özer, Process Biochem., **40**, 3559 (2005).

39. N. Kannan and M. Meenakshisundaram, Water, Air and Soil Poll., **138**, 289 (2001).

40. W. J. Weber, Wiely-Intersc., New York (1972) p. 199.

41. A. Ozer and G. Dursun, J. Hazard. Mater., **146**, 262 (2007).

42. K. R. Hall, L. C. Eagleton, A. Acrivos and T. Vermeulen, I & EC Fundam., **5**, 212 (1966).