Journal of Chemical Health Risks

Journal of Chemical Health Risks (2014) 4(1), 63–73

ORIGINAL ARTICLE

Equilibrium and Kinetic Studies of Direct Red 81 Biosorption onto Modified Silk Maze as an Economical Biosorbent

Mohammad Momen Heravi[1]*, Pouran Ardalan[2], Alireza Vafaie [1]

[1] Department of Chemistry, Mashhad Branch , Islamic Azad University, Mashhad, Iran

[2]Young Researchers Club, Mashhad Branch, Islamic Azad University, Mashhad, Iran

(Received: 22 October 2013 Accepted: 21 December 2013)

KEYWORDS

Biosorption
Direct red 81
Thermodynamic study
Kinetic models
Ultrasonic irradiation

ABSTRACT: In this study, the potential of biosorbent obtained from silk maze, was investigated for the batch biosorption of Direct red 81 (DR 81) in aqueous solution. The effects of temperature, biosorbent amount, contact time, initial dye concentration and ultrasonic irradiation were also evaluated. Furthermore, experimental equilibrium and kinetics data were fitted by Langmuir and Freundlich isotherms and pseudo-first-order and pseudo-second-order kinetic models, respectively. Kinetic experiments revealed that the biosorption of DR 81 onto modified silk maze can be described with a pseudo second-order model while the equilibrium isotherm data were well described by the Freundlich model. The negative thermodynamic values of $\Delta H^{o}$and ΔG^{o}showed that the biosorption is an endothermic process and occurs spontaneously in the nature.The results presented that this waste material may be a suitable biosorbent for removal of industrial effluents due to its low cost and high efficiency.

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 involving textile, paper, printing and dye houses. The generation of these products leads to the formation of wastewater contaminated with dyes. The textile industry is responsible for the use of about 30% of synthetic dyes [1]. Typical textile wastewater contains many types of dye molecules [2]. Many organic dyes are toxic to microorganisms and harmful to human beings. In the other hand, dye molecules have complex molecular of these products lead to the formation of wastewater contaminated with dyes. The textile industry is structures; they are very resistant to biodegradation [3, 5]. Hence, the treatment of effluents containing dyes has

*Corresponding author. : drmh@mshdiau.ac.ir(M. M. Heravi).

been a challenging problem among environmental technologies and it has always been necessary to find dye-removal efficient methods [6, 7]. Several methods have been reported for efficient removal of dyes from industrial wastewater, including, chemical precipitation [8], adsorption [9], electro-coagulation [10], biosorption [11, 12], electro-deposition [13] membrane systems [14], reverse osmosis and membrane filtration [15].The conventional methods for treatment of the wastewater usually suffer from some disadvantages, including complicated procedures, formation of by-products, expensive and energy-intensive, limited versatility and less adaptability to a wide range of dye wastewaters [16]. Recently, there has been a growing interest in finding low-cost, easily obtainable, highly efficient, and environmentally benign alternatives to the current expensive methods [17, 18]. One of the biological processes is biosorption method. Biosorption may be simply defined as the removal of substances from solution by biological material. Such substances can be organic and inorganic. The biosorption process involves a solid phase (sorbent or biosorbent; biological material) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (sorbate, dye moleculs) [19, 20].

The major advantages of biosorption 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 with the conventional biological process treatment [21, 22]. Therefore, in the recent decades, there has been an increasing interest to find cheaper and easily provided natural adsorbents which are compatible with the environment. Certain natural materials such as banana pith [23], rice husk [24], papaya seeds [25], orange peel, banana peel [26], Caulerparacemosa var. cylindracea [27], Caulerpalentillifera [28, 30], Posidoniaoceanica [31, 37], Camel Thorn Plant [38] and Chamomilla Plant [39] have been used for the treatment of wastewaters in previous studies. The present study aimed to present the usage of a natural environmental waste, silk maze, for the removal of dyes from industrial effluents. To obtain a better understanding of the biosorption mechanisms, the kinetic, isotherm and thermodynamic of dye removal were studied in batch system. Also, the effects of different parameters such as temperature, initial dye concentration, biosorbent dosage, contact time and ultrasonic irradiation were investigated on dye removal efficiency. Direct red was selected in this study as an azo-based dye model, which has been widely used in many industries.

MATERIALS AND METHODS

Materials

Direct red 81 ($C_{29}H_{19}N_5Na_2O_8S_2$) was purchased from Sigma–Aldrich Company, and was used without purification (Figure 1). Other chemical agents used were analytical-reagent grade and all the solutions were prepared with distilled water.

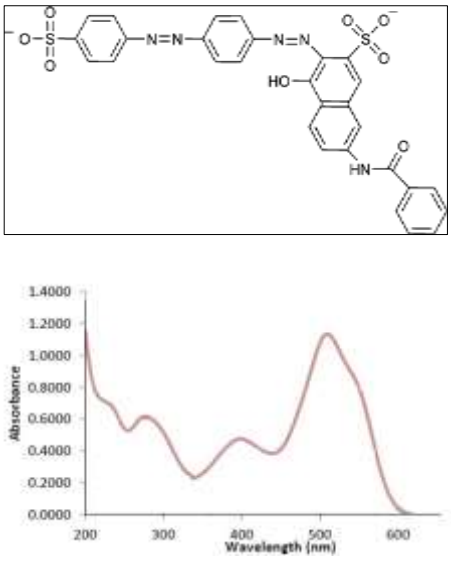

Figure1. The structure and UV Vis spectrum of DR 81

Preparation of biomass

The silk mazes were washed repeatedly with distilled water for removing dust, dried in an oven at 100°C and subsequently soaked in a H_3PO_4 solution for one day for protonation of biomass. Then, the biosorbent was filtered and heated until being dried. In the next step, the biosorbent was carbonized at 600°C for 20 minutes. The activated product was then cooled to room temperature. Finally, the dried biomass was ground and sieved to homogenous and fine small particles and stored in an air-tight polyethylene bottle.

Instrument

The residual DR 81 concentration was determined by using UV-Vis spectrophotometer (Perkin Elmer Lambda 25) at maximum wavelength of DR 81 (508 nm).

Batch experimental procedure

Batch biosorption experiments were performed on a mechanical stirrer using 500 mL beakers containing 250 mL of dye solutions. The influence of temperature, biosorbent dose, dye concentration and contact time, were optimized under the batch conditions. Kinetic studies at various temperatures of 25, 30, 35 and 40 °C under optimum conditions were conducted to verify the fitting of the experimental data to the first-order and the pseudo-second order kinetic models.

In order to analyze the biosorption equilibrium, we performed experiments changing initial dye concentration from 40 to 100 ppm. At the end of each experiment, the absorbances of the residual concentrations were measured by using the UV-Vis spectrophotometer.

Dye removal efficiency was computed through the following formula:

$$\%\text{Removal efficiency}\ \% = \frac{C_0 - C_f}{C_0} \times 100 \quad (1)$$

The amount of dye biosorbed onto unit weight of non-living sorbent, q_e (mg g^{-1}) was calculated using the mass balance equation given by:

$$q_e = (C_0 - C_f) \times \frac{V}{M} \quad (2)$$

Where q_e is the dye biosorption (mg g^{-1}), C_0 and C_f are the initial and equilibrium dye concentrations in the solution (ppm), respectively, V is the solution volume (L) and M is the biosorbent mass (g).

RESULTS AND DISCUSSION

The effect of contact time

The effect of contact time on the DR 81 removal by modified silk maze was studied by the variation of contact time from 10 to 70 min. for different initial dye concentrations of 40, 60, 80, 100 ppm with a biosorbent dosage equal to 1.5 g.

The effect of contact time on removal percentage of DR81 is shown in Figure 2. The results imply that the removal efficiency decreased from 97.7% to 60.3% with increase in the dye concentration from 40 to 100 ppm at the initial contact time of 30 min.

As can be seen, the contact time was an important parameter for the biosorption of the DR81 on modified silk maze. Subsequently, the removal efficiency of the DR81 reached to 97.7% and 95.2% at 70 min. for the initial dye concentrations of 40 and 100 ppm, respectively. A further increase in the contact time had a negligible effect on the efficiency of biosorption process. The adsorption of DR 81 on to modified silk maze was found to be rapid at initial period and then became slow and stagnated with increasing contact time (Figure 2). Thus, the dye adsorption by biosorbent was assumed to consist of three consecutive steps: (i) transport of adsorbate molecules from bulk solution to the exterior surface of adsorbent (film diffusion); (ii) transport of the adsorbate molecules within the pores of the adsorbent, which occured on the external surface (intra-particle diffusion or pore diffusion); (iii) sorption of the adsorbate molecules on the interior surfaces of the pores and capillary spaces of the adsorbent [40]. Of the three steps, the third step was very rapid and could not be a rate-controlling step [41] and [42].

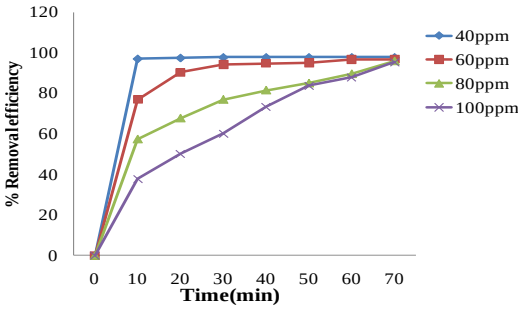

Figure 2. The effect of contact time on the DR81 removal by using 1.5 g modified silk maze (T=25°C)

In addition, Figure 3 shows dye biosorption at equilibrium (q_e) as well as the percent of removal efficiency over the range 40-100 ppm of initial concentrations.

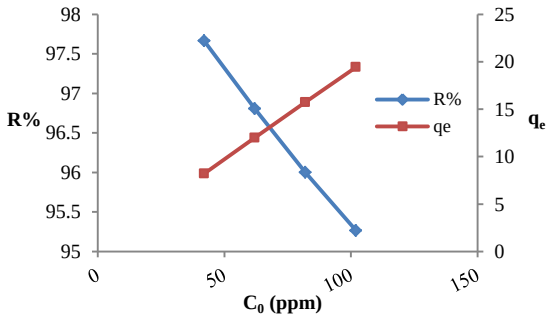

Figure 3.Biosorption plot at equilibrium (q_e) and removal efficiency percentage in different concentration

As can be seen, the dye removal efficiency decreased rapidly with increasing of initial concentration but $q_e$increased with increasing of initial concentration. In another part of this study, the kinetics data were analyzed using pseudo-first-order and pseudo-second-order kinetic models. The linear form of the pseudo-first-order rate equation can be defined as follows [43]:

$$\ln(q_e - q_t) = lnq_e - k_1 t \quad (3)$$

Where $q_e$and q_t are the amounts of dye biosorbed at equilibrium and at time t (mg g^{-1}), and k_1 is the first-order rate constant (min^{-1}) for the biosorption. The values of k_1 were calculated from the plot of $1/q_t$ versus 1/t (Figure 4).

The pseudo-second-order kinetic model expression [44] can be written as follows:

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{t}{q_e} \quad (4)$$

Where q_e and q_t are the amount of dye adsorbed at equilibrium and at time t, respectively (mg g^{-1}), and k_2 (g mg^{-1} min^{-1}) is the pseudo second-order rate constants. The values of k_2 were calculated from the plot of t/q_t versus t (Figure 5).

The linear regression coefficients close to 1 (Table 1) indicated that the biosorption of DR81 was fitted with the pseudo second order kinetics [45]. Also the Biosorption of Acid Orange 7 (AO7), C.I. Basic Red 46 (BR46) and C.I. Basic Blue 3 (BB3) dyes by green algal Spirogyra showed the similar results [46].

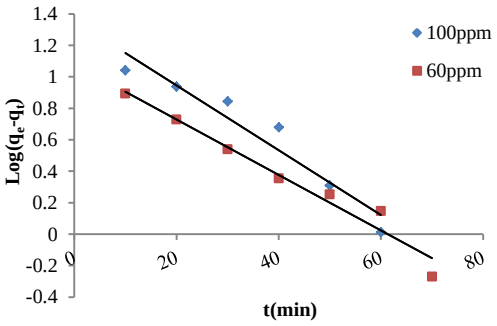

Figure 4. The pseudo first order kinetic plots for the biosorption of DR81 onto modified silk maze at different concentration (T=25°C)

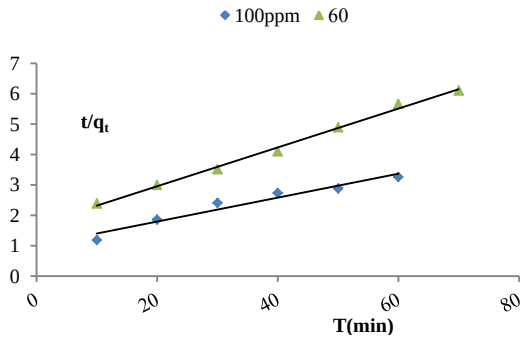

Figure 5. The pseudo second order kinetic plots for the biosorption of DR81 onto modified silk maze at different concentration (T=25°C)

Table 1. Kinetic parameters for biosorption of DR81 dye onto modified silk maze

Initial Concentration (ppm)	pseudo first order kinetic model		pseudo second order kinetic model	
	k_1 (min^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	R^2
60	4×10^{-2}	0.964	2.43×10^{-3}	0.996
100	4.7×10^{-2}	0.929	1.53×10^{-3}	0.993

The effect of biosorbent dosage

The effect of biosorbent dosage (1–2.5 g) was investigated on the biosorption of DR81 and the results are represented in Figure 6. As can be seen in this figure, dye removal efficiency increased rapidly with increasing of biosorbent until it reached the value of 98.9% hving the biomass content of 2 g.The increase in the removal rate of DR81 can be explained by the increased surface area of the biosorbent and availability of more binding sites for dye molecules [47].

On the other hand, further increase in the biosorbent dosage up to 2 g did not significantly change the biosorption yield. This was due to the binding of almost all dye ions to biosorbent surface and the maintenance of equilibrium between the dye molecules on the biosorbent and those present in the solution [48, 49].

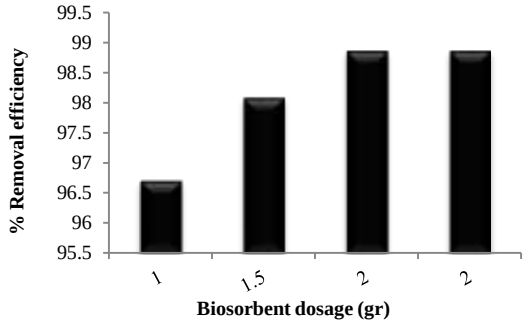

Figure 6. Effect of biosorbent dosage on removal efficiency of DR81 onto modified silk maze (T= 25 °C)

Biosorption isotherms

The results obtained from equilibrium isotherms were analyzed using Langmuir and Freundlich models. The Langmuir isotherm assumes a monolayer adsorption onto a solid surface with a definite number of identical sites. It can be considered as Eq. (5): [50]

$$\frac{C_e}{q_e} = \frac{1}{q_{max}.K} + \frac{C_e}{q_{max}} \qquad (5)$$

Where q_e (mg g^{-1}) and C_e (mg L^{-1}) are the amount of biosorbed dye per unit mass of biosorbent and unadsorbed dye concentration in solution at equilibrium, respectively.q_{max} is the maximum amount of the biosorbed dye per unit mass of biosorbent to form a complete monolayer on the surface bound at high C_e (mg g^{-1}), and K (L mg^{-1}) is a constant related to the affinity of the binding sites.

The Freundlich's adsorption isotherm model, which accounts for a multilayer heterogenous adsorption, is widely used to describe the dyes biosorption isotherm. It is stated by exponential equation as Eq. (6): [51]

$$\ln(q) = \ln(K_f) + \frac{1}{n}\ln(C) \qquad (6)$$

Where K_f (L g^{-1}) and 1/n are Freundlich isotherm constants related to biosorption capacity and intensity of biosorption, respectively. Figure 7 shows the linear plot of (log q_e versus log C_e) of Freundlich isotherm.

The Langmuir and Freundlich constants and regression coefficients for the DR81 biosorption are collected in Table 2. Based on the R^2 values the Freundlich isotherm is better in predicting the DR81 biosorption than the Langmuir isotherm (Figure 7). It is noteworthy that the Freundlich constant 1/n smaller than unity indicated that the biosorption process was favorable under the optimal experimental conditions [52]. The biosorption of Acid Black 1 onto marine brown macroalgae showed same results [53].

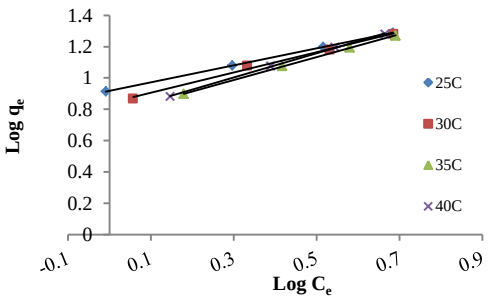

Figure 7.Freundlich isotherm plots for the biosorption of DR81 by modified silk maze at different temperatures

Table 2.Isotherm model parameters for the biosorption of DR81 onto modified silk maze.

T(K)	Freundlich isotherm			Langmuir isotherm		
	K_F	1/n	R^2	K_L	q_m	R^2
298	8.279	0.541	0.992	0.3548	30./30	0.985
303	6.934	0.646	0.993	0.2195	37.04	0.988
308	5.861	0.731	0.994	0.1304	47.62	0.983
313	5.902	0.772	0.989	0.1132	55.55	0.987

Thermodynamic studies

In order to describe the thermodynamic behavior of the biosorption of DR81 onto the modified silk maze, thermodynamic parameters were calculated including the change in free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) from the following equations (Table 3) [54]:

$$\Delta G^o = RTlnK \quad (7)$$

$$lnK = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (8)$$

Where R is the universal gas constant (8.314 J K^{-1} mol^{-1}), T is the absolute temperature (Kelvin) and K represents the equilibrium biosorption constants of the fitted isotherm. The values of ΔH^o and ΔS^o can be calculated from the slope and intercept of the linear plot of ln (K) versus 1/T (Figure 8).

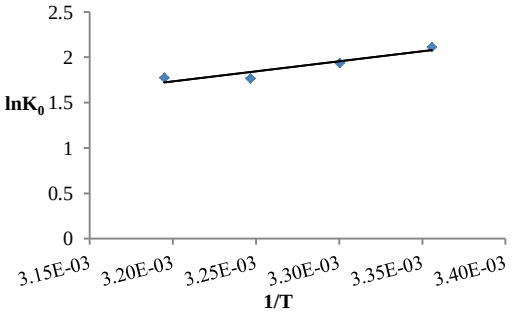

Figure 8.The plot of ln K versus 1/T for estimation of thermodynamic parameters for thebiosorption of DR81 onto the modified silk maze.

Table 3. Thermodynamic parametersforbiosorption of DR81 onto modified silk maze

T(K)	ΔG^{o}(kJ/mol)	ΔH^{o}(kJ/mol)	ΔS^{o}(kJ/K mol)
298	-5.15		
303	-4.93		
308	-4.70	-18.44	-44.61
313	-4.48		

The negative values of ΔG° indicate that the DR81 biosorption onto modified silk maze was spontaneous and feasible at all the studied temperatures (25, 30, 35 and 40 °C). It was noted that the change in free energy for physical sorption was between −20 and 0 kJ mol^{-1}, but it was over the range −80 to −400 kJ mol^{-1} for the chemical sorption step. In addition, biosorption of DR 81 onto modified silk maze was a physical sorption process. Moreover, the negative value of ΔH° (−9.74 kJ mol^{-1}) indicates that biosorption followed an exothermic process [55, 56]. The negative value of ΔS° also suggests decreased randomness at the solid/solution interface during the DR81 biosorption onto modified silk maze.

Effect of ultrasonic irradiations on biosorption of DR81 onto modified silk maze

The effect of ultrasonic irradiations on biosorption was studied by equipment operating at 40 kHz (DSA100-SK_2-4.0L). This biosorption experiment was performed by adding 1.5 g of biosorbent into a beaker containing 250 mL of initial concentrations 100 ppm of dye solution. These concentrations and biosorbent amount were selected because ultrasonic irradiation removed completely the DR81 in ten minutes with higher dose of biosorbent and lower concentration. Figure 9 indicates the effect of ultrasonic irradiations on the removal efficiency of DR 81 on to biosorbent.As can be seen, the removal efficiency increased with using the ultrasonic irradiations from 95.6% to 99.2% in 70 minutes. Moreover, the results show that removal efficiency was increased from 74.5% to 95.3% by using ultrasonic irradiation at the initial 30 minutes of contact time. This could be justified regarding the fact that at the presence of ultrasonic irradiations, there are more bubbles and also the bubbles collapse more violently. This behavior can lead to more considerable effects on the biosorption process [57].

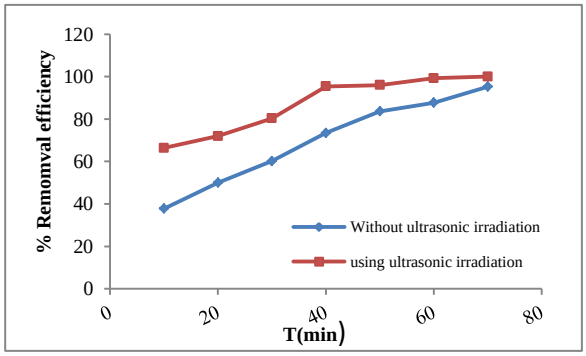

Figure9.Effect of ultrasonic irradiations on removal efficiency of Direct red 81 on modified silk maze (dye concentration=100 ppm; biosorbent dosage= 1.5 g; T= 298K).

Activation energy

Arrhenius equation [58] was fitted by the use of pseudo-second-order rate constant to determine activation energy (E_a) for the biosorption of DR81 onto modified silk maze. The Arrhenius equation is expressed as:

$$lnk = lnA - \frac{E_a}{RT} (9)$$

Where k is pseudo second order rate constant, A is the Arrhenius pre exponential factor or Arrhenius constant. The units of the pre-exponential factor A are identical to those of the rate constant and will vary depending on the order of the reaction and is the total number of collisions (leading to a reaction or not) per second, E_a is the activation energy (kJ mol^{-1}), R is the universal gas constant (8.314 J mol^{-1} K^{-1}), and T is the absolute temperature (K). The type of biosorption can be estimated by the magnitude of activation energy. Generally, low activation energies (5–50 kJ mol^{-1}) are characteristics of physisorption, while higher activation

energies (60–800 kJ mol^{-1}) suggest chemisorption (chemical adsorption) [59]. Activation energy for the biosorption of DR81 onto modified silk maze was 48.24 kJ mol^{-1}, suggesting that the biosorption process could be mainly physisorption (physical biosorption) [60, 61].

CONCLUSION

In this study, the modified silk maze was used to biosorb DR81 from aqueous solution. The effects of different parameters such as temperature, biosorbent amount, contact time, initial dye concentration and ultrasonic irradiation were evaluated on removal efficiency. It was observed that the modified silk maze had maximum monolayer adsorption capacity, 55.5 mg/g. The Langmuir and Freundlich isotherms were well fitted with the experimental values. Based on the R^2 values the Freundlich isotherm is better in predicting the DR81 biosorption than the Langmuir isotherm.

The thermodynamic studies showed that the biosorption process was spontaneous and exothermic since the negative ΔG^o value and negative ΔH^o value. Also the biosorption of DR81 onto modified silk maze well agreed with the pseudo-second-order kinetic model (R^2 = 0.996). In addition activation energy for the biosorption of DR81 onto modified silk maze was 48.24 kJ mol^{-1}, suggesting that the biosorption process could be mainly physisorption. Also the effect of ultrasonic irradiations was studied on biosorption. The results showed removal efficiency increased with using the ultrasonic irradiations from 95.6% to 99.2% in 70 minutes

REFERENCES

1. Hessel C., Allegre C., Maisseu M., Charbit F., Moulin P., 2007. Guidelines and legislation for dye house effluentsJournal of Environmental Management. 83, 171-180.

2. Phalakornkule C., Polgumhang S., Tongdaung W., Karakat B., Nuyut T., 2009. Electrocoagulation of blue reactive, red disperse and mixed dyes, and application in treating textile effluent. Journal of Environmental Management. 91(4): 918-926.

3. Saeed A., Sharif M., Iqbal M., 2010. Application potential of grapefruit peel as dye sorbent: kinetics, equilibrium and mechanism of crystal violet adsorption.Journal of Hazardous Materials. 179, 564-572.

4. Uddin M.T., Rukanuzzaman M., Khan M.R., Islam M. A., 2009. Jackfruit (Artocarpusheterophyllus) leaf powder: An effective adsorbent for removal of methylene blue from aqueous solutions. Journal of Environmental Management. 90 (2): 3443-3449.

5. Mona S., Kaushik A., Kaushik C.P., 2011. Biosorption of reactive dye by waste biomass of Nostoclinckia.International Biodeterioation and Biodegradation. 37 (10): 1581- 1594.

6. Khataee A.R., Dehghan G., 2011. Optimization of biological treatment of a dye solution by macroalgaeCladophora sp. using response surface methodology.Journal of the Taiwan Institute of Chemical Engineers. 42, 26-33.

7. Soon A.N., Hameed B.H., 2011. Heterogeneous catalytic treatment of synthetic dyes in aqueous media using Fenton and photo-assisted Fenton process. Desalination. 269, 1-16.

8. Zhu M. X., Lee L., Wang H., Wang Z., 2007. Removal of an anionic dye by adsorption/precipitation processes using alkaline white mud. Journal of Hazardous Materials. 149, 735- 741.

9. Eren Z., Acar F.N., 2006. Adsorption of Reactive Black 5 from an aqueous solution: equilibrium and kinetic studies. Desalination. 194, 1-10.

10. Sengil A., Ozacar M., 2009. The decolorization of C.I. Reactive black 5 in aqueous solution by electrocoagulation using sacrificial iron electrodes.Journal of Hazardous Materials. 161(2): 1369-1376.

11. Barron-Zambrano J., Szygula A., Ruiz M., Sastre A M., Guibal E., 2010. Biosorption of Reactive Black 5 from aqueous solutions by chitosan: column studies. Journal of Environmental Managment. 91, 2669-2675.

12. Aksu Z., 2001. Biosorption of reactive dyes by dried activated sludge: equilibrium and kinetic modeling. Biochemical Engineering Journal. 7, 79-84.

13. Regan B., Schwartz D.T., 1995. Efficient photo-hole injection from adsorbed cyanine dyes into electrodeposited Copper (I) Thiocyanate thin films. Chemistry of Materials. 7, 1349- 1354.

14. Nataraj S.K. Hosamani K.M., Aminabhavi T.M, 2009. Nanofiltration and reverse osmosis thin film composite membrane module for the removal of dye and salts from the simulated mixtures. Desalination. 249 (1): 12-17.

15. Eiteman M., 1998. Evaluation of membrane filtration and ozonation processes for treatment of reactive-dye wastewater. Journal of Environmental Engineering. 124 (3): 272- 277.

16. Kaushik P., Malik A., 2009. Fungal dye decolourization: Recent advances and future potential dye. Environment International. 35, 127- 141.

17. Chen K C., Wu I.Y., Liou D.J., Hwang S.C., 2003. Decolorization of the textile dyes by newly isolated bacterial strains. Journal of Biotechnology. 101(1): 57-68.

18. Nemr A.E., Abdelwahab O., Sikaily A.E., Khaled A., 2008. Removal of direct blue-86 from aqueous solution by new activated carbon developed from orange peel.Journal of Hazardous Materials. 161, 102-110.

19. Geoffrey Michael G., 2008. Biosorption: critical review of scientific rationale, environmental importanceand significance for pollution treatment, Published online in Wiley Interscience.

20. Ahalya N., Ramachandra T.V., Kanamadi, R.D., 2003. Biosorption of Heavy Metals, Res. Journal of Chemical Environment. 7, 71- 78.

21. Ansari R., Mosayebzadeh Z., 2010. Removal of basic dye methylene blue from aqueous solutions using sawdust and sawdust coated with polypyrrole. Journal of Iranian Chemical Society.7, 339- 350.

22. Schiewer S., Wong M.H., 2000. Ionic strength effects in biosorption of metals by marine algae. Chemosphere. 41(1): 271- 282.

23. Namasivayam C., Prabha D., Kumutha M., 1998. Removal of Direct Red and Acid Brilliant Blue by Adsorption on to Banana Pith. Bioresource Technology. 64 (1): 77-79.

24. McKay G., Porter J.F., Prasad G.R., 1999. The Removal of Dye Colours from Aqueous Solutions by Adsorption on Low-cost Materials. Water Air Soil Poll. 114 (3): 423-438.

25. Hameed B., 2009. Evaluation of papaya seeds as a novel non-conventional low cost adsorbent for removal of methylene blue. Journal of Hazardous Materials.162, 939- 944.

26. Annadurai G., Juang R., Lee D., 2002. Use of cellulose-based wastes for adsorption of dyes from aqueous solutions. Journal of Hazardous Materials.Journal of Hazardous Materials. 92 (3): 263-271.

27. Cengiz S., Cavas L.L., 2008. Removal of methylene blue by invasive marine seaweed: Caulerparacemosa var. cylindracea. BioresourceTechnology. 99(7): 2357-2367.

28. Marungrueng K., Pavasant P., 2006. Removal of basic dye (Astrazon Blue FGRL) using macroalga Caulerpalentillifera. Journal of Environmental Management. 78, 268-274.

29. Marungrueng K., Pavasant P., 2007. High performance biosorpbent (Caulerpalentillifera) for basic dye removal.Bioresource Technology. 98, 1567- 1572.

30. Pavasant P., Apiratikul R., Sungkhum V., Suthiparinyanont P., Wattanachira S., Marhaba T.F., 2006. Biosorption of Cu^{2+}, Cd^{2+}, Pb^{2+}, and Zn^{2+} using dried marine green macroalga Caulerpalentillifera. Bioresource Technology. 97, 2321-2329.

31. Ncibi M.C., Mahjoub B., Seffen M., 2007. Kinetic and equilibrium studies of methylene blue biosorption by Posidoniaoceanica (L.) fibres. Journal of Hazardous Materials.139, 280- 285.

32. Ncibi M.C., Mahjoub B., Seffen M., 2008. Investigation of the sorption mechanisms of metal-complexed dye onto Posidoniaoceanica (L.) fibres through kinetic modelling analysis. Bioresource Technology. 99, 5582–5589.

33. Ncibi M.C., Mahjoub B., Ben Hamissa A.M., Ben Mansour R., Seffen M., 2008. Biosorption of textile metal-complexed dye from aqueous medium using Posidoniaoceanica (L.) leaf sheaths: Mathematical modelling. Desalination. 3,109- 121.

34. Guezguez S., Dridi-Dhaouadi F., 2009. Sorption of Yellow 59 on Posidoniaoceanica, a non-conventional biosorbent:comparison with activated carbons. Industrial Crop Productions. 29, 194- 204.

35. Cengiz S., Cavas L., 2010. A promising evaluation method for dead leaves of Posidoniaoceanica (L.) in the adsorption of methyl violet. Marine Biotechnology. 12 (6): 728- 736.

36. Cavas L., Karabay Z., Alyuruk H., Doˇgan H., Demir G.K., 2011. Thomas and artificial neural network models for the fixed-bed adsorption of methylene blue by a beach waste Posidoniaoceanica (L.) dead leaves.. Chemical Engineering Journal. 71, 557-562.

37. Dural U., Cavas L., Katsaros F., Papageorgiou S., 2011. Methylene blue adsorption on activated carbon prepared from Posidoniaoceanica (L.) dead leaves. Chemical Engineering Journal. 168 (1): 77- 85.

38. Moghadasi F., Momen Heravi M., Bozorgmehr M. R., Ardalan P., Ardalan T., 2010. Kinetic and Thermodynamic Study on the Removal of Methyl Orange from Aqueous Solution by Adsorption onto Camel Thorn Plant. Asian Journal of Chemistry. 22 (7): 5093-5100.

39. Momen Heravi M., Kodabande A., Bozorgmehr M. R., Ardalan T., Ardalan P., 2012. Kinetic and Thermodynamic Studies on Biosorption of Direct Red 81 from Aqueous Solutions by ChamomillaPlant. Journal of Chemical Health Risks. 4(2): 37.

40. Ma F., Yu L. Zhou L., Jin M.X. Yang J.S., Luan Y.H., Tang H.B., Fan Z.W., Yuan J.H., 2012. Enhanced adsorption removal of methyl orange and methylene blue from aqueous solution by alkali-activated multiwalled carbon nanotubes.Applied Materials and Interfaces. 4, 5749–5760

41. Arami M., Limaee N.Y., Mahmoodi N.M., Tabrizi N. S., 2006. Equilibrium and kinetics studies for the adsorption of direct and acid dyes from aqueous solution by soy meal hull. Journal of Hazardous Materials. 135, 171–179.

42. Gupta V.K., Mittal A., Gajbe V., Mittal J., 2008. Adsorption of basic fuchsin using materials – bottom ash and deoiled soya – as adsorbents.Journal of Colloid and Interface Science. 319, 30–39

43. Azizian S., 2004. Kinetic models of sorption: a theoretical analysis. Journal of Colloid and Interface Science. 276 (1): 47- 52.

44. Ho Y.S., McKay G., 1998. Kinetic models for the sorption of dye from aqueous solution by wood. Journal of Environmental Science Health B. 76, 183- 191.

45. SibelTunaliAkar A., SafaÖzcan B., Tamer Akar A., Adnan Özcan B., ZerrinKaynak C., 2009. Biosorption of a reactive textile dye from aqueous solutions utilizing an agro-waste, Desalination. 249, 757–761.

46. Khataee A.R., Vafaei F., Jannatkhah M., 2013. Biosorption of three textile dyes from contaminated water by filamentous green algal Spirogyra sp.: Kinetic,

isotherm and thermodynamic studies, International. Biodeterioration Biodegradation. 83, 33- 40.

47. Akar T., Tosun I., Kaynak Z., Kavas E., Incirkus G., Akar ST., 2009. Assessment of the biosorption characteristics of a macro-fungus for the decolorization of Acid Red 44 (AR44) dye. Journal of Hazardous Materials. 171(1): 865- 871.

48. Akkaya G., Özer A., 2005. Biosorption of Acid Red 274 (AR 274) on Dicranellavaria: Determination of equilibrium and kinetic model parameters. Process Biochemistry. 40, 3559- 3568.

49. Bai R. S., Abraham T.E., 2001. Biosorption of Cr (VI) from aqueous solution by Rhizopusnigricans BioresourceTechnology.79, 73- 81.

50. Langmuir I., 1918. Langmuir "Adsorption of Gases on Plain Surfaces of Glass Mica Platinum. Journal of American Chemical Society. 40 (9):1361- 1403.

51. Freundlich H.M.F., 1906. Uber die adsorption in losungen. Zeitschriftfür Physikalische Chemie. 57,385- 470.

52. Senturk H.B., Ozdes D., Duran C., 2010. iosorption of Rhodamine 6G from aqueous solutions onto almond shell (Prunusdulcis) as a low cost biosorbent. Desalination. 252 (1): 81- 87.

53. Daneshvar E., Kousha M.A., Jokar M., Koutahzadeh N., Guibal E., 2012. Acidic dye biosorption onto marine brown macroalgae: Isotherms, kinetic and thermodynamic studies. Chemical Engineering Journal. 204, 225–234.

54**.** Aravindhan R., Rao J.R., Nair B.U., 2007. Removal of basic yellow dye from aqueous solution by sorption on green alga Caulerpascalpelliformis. Journal of Hazardous Materials. 142, 68–76.

55. Özcan A., Özcan A.S., 2005. Adsorption of Acid Red 57 from aqueous solutions onto surfactant-modified sepiolite. Journal of Hazardous Materials. 125, 252- 259.

56. Özcan A.S, Erdem B., Özcan A., 2005. Adsorption of Acid Blue 193 from aqueous solutions onto BTMA-bentonite. Colloid Surface A. 266 (1): 73- 81.

57. Entezari M.H., Rohani Bastami T., 2006. Sono-sorption as a new method for the removal of lead ion from aqueous solution. Journal of Hazardous Materials. 137, 959- 964.

58. Anirudhan T.S., Radhakrishnan P.G., 2008. Thermodynamic and kinetic of adsorption of cu (II) from aqueous solution on to a new cationic exchanger derived from Taman ad fruit shell. Journal of Chemical. Thermodynamic. 40,702- 709.

59. Deniz F., Karaman S., 2011. Removal of Basic Red 46 dye from aqueous solution by pine tree leaves. Chemical Engineering Journal. 170, 67- 74.

60. Oura K., Surface Science, An Introduction, 1st ed., Springer: Berlin, 2003

61. Hans L., Surfaces and interfaces of solids, fifth ed., Springer: Verlag, 1993.