Research Article

Adsorption of Acid Red 88 dyes using Single-walled Carbon Nanotubes (SWCNTs)

Davoud Balarak[1], Masomeh Ebrahimi[2], Ferdos Kord Mostafapour[1], Bijan Nouri[3], Shahram Sadeghi*[4]

[1]Department of Environmental Health, Health Promotion Research Center, Zahedan University of Medical Sciences, Zahedan, Iran
[2]Department of Environmental Health Engineering, Tabriz University of Medical Sciences, Tabriz, Iran
[3]Social Determinants of Health Research Center, Kurdistan University of Medical Sciences, Sanandaj, Iran
[4]Student Research Committee, Kurdistan University of Medical Sciences, Sanandaj, Iran

Abstract Single-walled Carbon Nanotubes (SWCNTs) used as absorbents to remove Acid Red 88 (AR88) dyes from wastewater have been investigated here because they are effective in removing organic pollutants. The adsorption process was affected by various experimental conditions such as pH, contact time and biosorbent concentration. Maximum dye removal was observed at pH 3 and 0.25 g/L o biosorbent concentration. Adsorption equilibrium was established in 75 min. Experimental data were fitted well to the Langmuir isotherm model. The maximum dye removal percentage was determined as 97.5%. The negative values of free-energy change confirmed the feasibility of the process and the spontaneous nature of adsorption. Furthermore, from the magnitude of ΔH, the process was found to be endothermic physisorption.

Keywords Acid Red 88, Adsorption, SWCNTs, Isotherm, Thermodynamics

Introduction

Industrial effluents are one of the major causes of environmental pollution because effluents discharged from dyeing industries are highly colored with a large amount of suspended organic solid [1-2]. Dyes are colour organic compounds which can colorize other substances [3,-4]. These substances are usually present in the effluent water of many industries, such as textiles, leather, paper, printing, and cosmetics [5-6]. The complex aromatic structures of dyes make them more stable and more difficult to remove from the effluents discharged into water bodies [7-8].

Dyes can be classified as anionic (acid dyes), cationic (basic dyes), and non-ionic (disperse dyes) [9]. Acid dyes are organic sulfonic acids; the commercially available forms are usually sodium salts, which exhibit good water solubility [10]. In sequence of their importance, acid dyes are mostly used with certain fiber types such as polyamide, wool, silk, modified acrylic, and polypropylene fibers as well as blends of the aforementioned fibers with other fibers such as cotton, rayon, polyester, regular acrylic [11-12].

Effluent from the dyeing industry contain highly coloured species; such highly coloured wastes are not only aesthetically displeasing but also hinder light penetration and may in consequence disturb biological processes in water-bodies [13-14]. In addition, dyes are toxic to some organisms and hence harmful to aquatic animals. Furthermore, the expanded uses of dyes have shown that some of them and their reaction products such as aromatic amines are highly carcinogenic [15-16]. Therefore, removal of dyes before disposal of the wastewater is necessary.

Most of the used dyes are stable to photodegradation, biodegradation and oxidizing agents. Currently, several physical or chemical processes are used to treat dye wastewaters [17-18]. However, these processes are costly and cannot effectively be used to treat the wide range of dye wastewater [19-20]. Adsorption has been found to be superior to other techniques for treating wastewater: it is low-cost, highly efficient, simple, easy to perform and insensitive to toxic substances [21]. Moreover, liquid-phase adsorption has been demonstrated to be highly efficient

in removing dyes from waste effluent. Hence, adsorption was selected herein as the approach used to treat reactive dye wastewater [22-23].

Carbon nanotubes (CNTs), with nano-sized diameter and tubular microstructure, have been the worldwide hotspot of study since their discovery because of their unique morphologies and various potential applications. Because of their relatively large specific surface areas and easily modified surfaces, much attention has been paid to the adsorption by CNTs of contaminants such as Zn^{2+}, Cd^{2+}, Pb^{2+}, also fluoride and antibiotics [24-29]. Therefore, CNTs might be ideal sorbents for the removal of dyes from water. The aim of this research was to use of SWCNTs for adsorption AR88 dye from the aqueous environments. The effect of various parameters Such as pH, contact time, adsorbent dose, initial dye concentration and temperature was studied on the dye removal efficiency.

Materials and Methods
Materials: Acid Red 88 dyes dye was purchased from AlvanSabet Co (Iran). The chemical structure and characteristics of AR88 are presented in Fig 1 and Table 1, respectively. Other chemicals including citric acid, sulfuric acid and sodium hydroxide were provided from Merck Co (Germany).

SWCNTs provided from Research Institute of Petroleum Industry (RIPI), Tehran, Iran. On the basis of the information provided by the manufacturer, the SWCNTs were synthesized by catalytic chemical vapor deposition (CVD) method. The size and morphology of SWCNTs were examined by scanning electron microscope (JEOL JSM 6500F) and transmission electron microscopy (TEM) (using a Philips XL30).

Adsorption experiments
The adsorption experiments were conducted in a batch system at room temperature (25 $^{\circ}$C) with 100 mL of the dye solution (100 mg/L) into a 250 mL Erlen Myer and agitated by an orbital shaker (180 rpm for 3 hr) at pH 7. After agitation, the suspensions were centrifuged (3600 rpm for 15 min) and the clear solution was analyzed for dye by an UV-Vis spectrophotometer (DR-5000 Hach) at maximum absorbance wavelength of 503 nm. All the experiments were conducted in duplicates and the mean values were applied. The removal efficiency and sorption capacity of the SWCNTs were determined by Eq. (1) and (2), respectively [30-32]:

$$q_e = (C_0 - C_e)\frac{V}{M}$$
$$R\% = \frac{C_0 - C_e}{C_0} \times 100$$

Where; R (%) and q_e (mg/g) are the removal efficiency and adsorption capacity, respectively. C_o (mg/L) is the initial dye concentration, C_e (mg/L) is dye concentration at the equilibrium, m (g) is the mass of the sorbent and V (L) is the volume of the dye solution.

Table 1: General characteristics of Acid Red 88

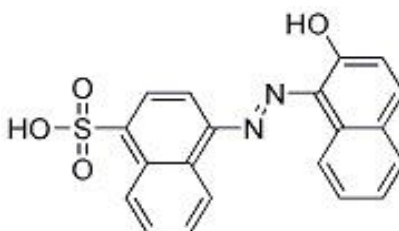| Generic name	Chemical formula	Molecular weight	λ_{max} (nm)	EC number
Acid Red 88	$C_{20}H_{13}N_2NaO_4S$	400.39 (g/mol)	503	216-760-3

Figure 1: The chemical structures of AR88

Results and Discussion
Figures 2a and 2b show the SEM and TEM images of SWCNT S. The size of the outer diameter for theSWCNTs was 7–20 nm. The length of SWCNTs was 10 μm. Furthermore, specific surface area of SWCNTs was more than 712.5 m^2/g, and the mass ratio of the amorphous carbon of SWCNTs was less than 5%.

Effects of pH and adsorbent dosage
The effect of pH for the adsorption of AR88 onto SWCNTs at 20 8C is shown in Fig. 3. It can be seen that the adsorption of AR88 was pH-dependent. The results show that the amount of adsorbed dye onto SWCNTs decreases as the pH increases from 3 to 11. This situation can be related to the surface charge of the adsorbent. SWCNTs has

negatively charged adsorption sites, but it is positively charged at low pH values. Therefore the electrostatic interactions between negatively charged $-SO^{-3}$ groups in the dye molecule and the positively charged adsorbent increase [33-35]. As a result, the amount of dye molecules onto the modified bentonite increases at lower pH values. In order to determine the effect of the biosorbent dosage on the biosorption efficiency of AR88, the amounts of biosorbent added into the biosorption medium were varied from 0.05 to 0.5 g/L and the results are presented in Fig 4. With increase in the biosorbent dosage, from 0.05 to 0.25 g/L, the percentage decolorization of AR88 increased from 36.40% to 97.5%, which is the maximum value obtained as the number of possible binding sites increased [36-37]. Further increase up to 0.5 g/L did not change the maximum AR88 biosorption capacity of the biosorbent and it almost stayed constant (p>0.05). This is because, at higher biosorbent concentrations, there is a very fast biosorption onto the biosorbent surface that produces a lower solute concentration in the solution than when the biosorbent concentration is lower [38-40].
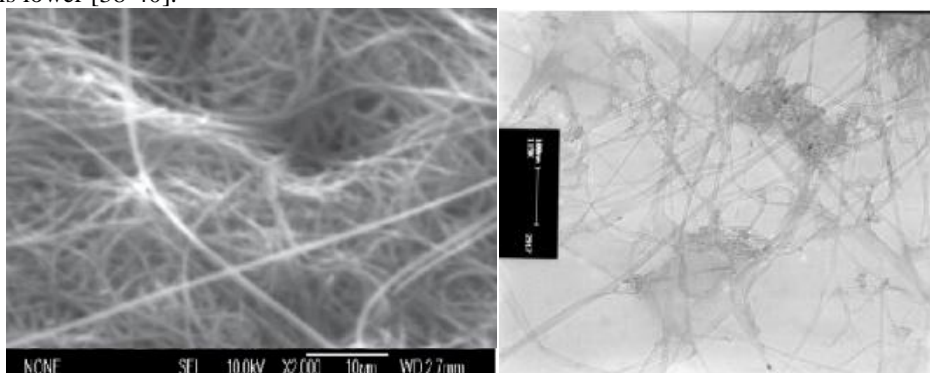

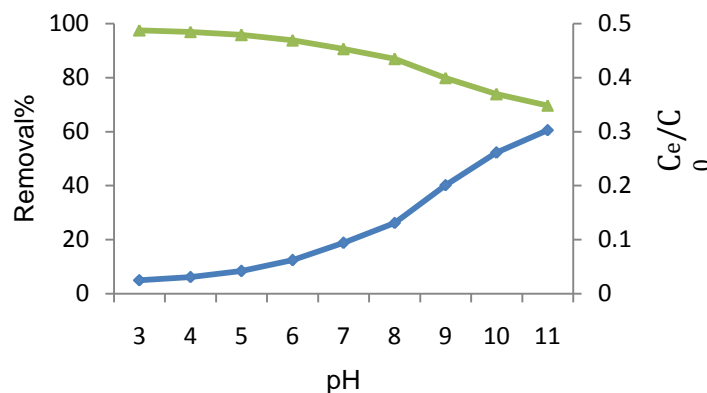*Figure 2: Micrographs of SWCNTs (a) SEM and (b) TEM*

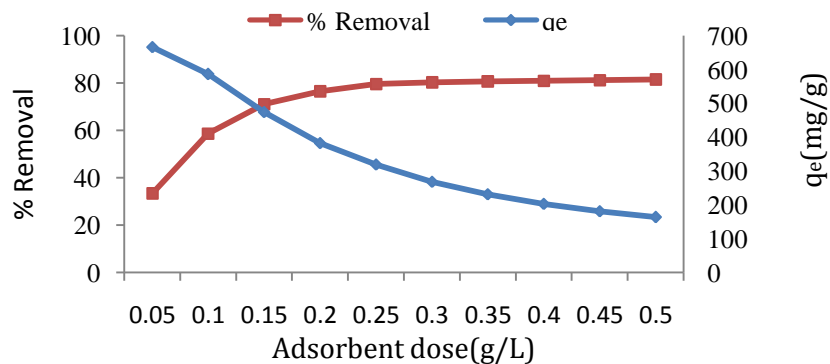*Figure 3: Effect of pH on AR88 removal (dose= 3 g/L, C_0 = 50 mg/L, time 90 min, temp= 28 ± 2 ℃)*

Figure 4: Effect of adsorbent dosage on AR88 adsorption. (C_0 = 100 mg/L, time = 90 min, pH = 3, temp= 28 ± 2 ℃)

Adsorption Isotherm

Adsorption isotherm models were widely applied to investigate the adsorption process. To better elucidate the mechanism of AR88 adsorption onto SWCNTs, three adsorption isotherms including Langmuir, Freundlich and Temkin isotherm models were used to fit the experimental equilibrium adsorption data [41-44]:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} \times \frac{C_e}{q_m}$$

$$\text{Ln } q_e = \ln K_F + \frac{1}{n} \ln Ce$$

$$q_e = \frac{Rt}{B} \ln K_T + \frac{RT}{b} \ln Ce$$

Where q_e (mg/g) and C_e (mg/L) are the equilibrium concentrations of AR88 in the liquid and solid phases, respectively; K_L (L/mg) represents the Langmuir isotherm constant that relates to the affinity of binding sites which describes the intensity of the adsorption process; q_m (mg/g) is the theoretical maximum adsorption capacity; K_F (mg/g) and n are Freundlich isotherm constants which can be regarded as adsorption capacity and intensity, respectively; A (L/g), R (8.314 J/mol K), and T (K) are Temkin constant related to equilibrium binding constant, gas constant and absolute temperature, respectively. b is heat of sorption, B= RT/b.

The temperature influence is an important controlling factor in the real applications of the dye removal process. The adsorption parameters of Langmuir, Freundlich and Temkin adsorption isotherms models at different temperatures of 20 °C, 30 °C and 40 °C were listed in Table 1. The experimental data on AR88 equilibrium adsorption onto SWCNTs were fitted by above mentioned three isotherm models. It was apparent that the Langmuir isotherm was found to fit quite well with the experimental data of the AR88 on SWCNTs in comparison with Freundlich and Temkin isotherm, also having the highest correlation coefficients (R^2), reflecting that the adsorption process belong to the monolayer adsorption and the adsorption sites are evenly distributed [45-47]. These facts confirm that the adsorption of AR88 onto the internal and external surface of SWCNTs involves the monolayer adsorption coverage of the AR88 on the surface of the adsorbent.

The adsorption capacity increased with increase of the temperature, indicating that the adsorption is endothermic, which was further explained by evaluation of thermodynamic parameters. The thermodynamic parameters, including standard Gibbs free energy change (ΔG^0, kJ/mol), standard enthalpy change (ΔH^0, kJ/mol) and standard entropy change (ΔS^0, kJ/mol K) were calculated to gain further insights into the adsorption mechanism of AR88 on the SWCNTs. The thermodynamic parameters of adsorption are expressed as [48-49]:

$$\Delta G^0 = -RT \ln K$$
$$\ln(K) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

Thermodynamic parameters were listed in Table 2. It can be seen that the positive values of (ΔH^0 confirmed the endothermic nature of the adsorption process. The negative values of ΔG^0 indicated the adsorptive performance of AR88 on the SWCNTs were feasible and spontaneous.

Table 1: The adsorption isotherms constants for the removal AR88 dye

Tem (°K)	Langmuir model			Freundlich model			Temkin model		
	q_m	K_L	R^2	n	K_F	R^2	B	K_T	R^2
293	214.32	0.172	0.997	2.38	45.11	0.922	69.44	0.061	0.899
303	219.48	0.294	0.999	2.89	56.37	0.894	106.2	0.077	0.915
313	223.71	0.375	0.995	3.45	64.25	0.907	141.5	0.095	0.937

Table 2: Thermodynamic parameters for the adsorption of AR88

Temperature (K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol K)
293	-1.85		
303	-2.74	12.74	0.014
313	-3.36		

Conclusion

The decolorization potential of textile dye AR88 by SWCNTs sorbent has been investigated as a function of initial pH, contact time, biosorbent and temperature in a batch system. Maximum dye adsorption capacity at 412.7 mg/L was observed at pH 3 and 0.25 g/L of sorbent concentration. The equilibrium data followed Langmuir, Freundlich and Temkin isotherm models at 20, 30 and 40 °C. An increase in the biosorption capacity of SWCNTs with temperature showed that the decolorization process is endothermic. Results indicated that SWCNTs was an effective candidate for textile dye AR88 removal from aqueous solutions.

Acknowledgements

References

1. Diyanati Tilaki RA, Balarak D, Ghasemi M. Removal of acid orang 7 (AO7) dye from aqueous solution by using of adsorption on to rice stem waste: kinetic and equilibrium study. Iranian journal of health sciences. 2014; 2(1):51-61

2. Balarak D, Mahdavi Y. Experimental and Kinetic Studies on Acid Red 88 Dye (AR88) Adsorption by Azolla filiculoides. Biochemistry & Physiology. 2016, 5:1

3. Cengiz S, Tanrikulu F, Aksu S. An alternative source of adsorbent for the removal of dyes from textile waters: Posidonia oceanica (L): Chemical Engineering Journal. 2012; 189–190; 32– 40.

4. Moussavi GR, Mahmoudi M. Degradation and biodegradability improvement of the reactive red 198 azo dye using catalytic ozonation with MgO nanocrystals. Chemical Engineering Journal. 2009. 152; 1–7.

5. Zazouli MA, Balarak D, Mahdavi Y. Application of Canola Residuals in Absorption of Reactive Red 198 (RR198) Dye from Aqueous Solutions. J Neyshabur Univ Med Sci 2014, 2(3): 56-66.

6. Robinson T,Chandran B, Nigam P. Removal of dyes from a synthetic textile dye effluent by adsorption on apple pomace and wheat straw. Water Research. 2002; 36,2824–2830.

7. Balarak D, Jaafari J, Hassani G, Mahdavi Y, Tyagi I, Agarwal S, Gupta VK. The use of low-cost adsorbent (Canola residues) for the adsorption of methylene blue from aqueous solution: Isotherm, kinetic and thermodynamic studies.Colloids and Interface Science Communications. Colloids and Interface Science Communications.2015; 7;16–19.

8. Zazouli MA, Yazdani J, Balarak D, Ebrahimi M, Mahdavi Y. Removal Acid Blue 113 from Aqueous Solution by Canola. Journal of Mazandaran University Medical Science. 2013;23(2):73-81.

9. Balarak D, Mahdavi Y , Bazrafshan E , Mahvi AH. Kinetic, isotherms and thermodynamic modeling for adsorption of acid blue 92 from aqueous solution by modified azolla filicoloides. Fresenius Environmental Bulletin.2016;25(5); 1321-1330.

10. Ozcan A, Omeroglu C, Erdogan Y, Safa Ozcan A. Modification of bentonite with a cationic surfactant: An adsorption study of textile dye Reactive Blue 19. Journal of Hazardous Materials. 2007; 140;173–179.

11. Tan C-y, Li G, Lu X-Q, Chen Z-l. Biosorption of Basic Orange using dried A. filiculoides. Ecol Engin. 2010; 5(36):1333–40.

12. Ali NF, El-Mohamedy RSR. Microbial decolourization of textile waste water.Journal of Saudi Chemical Society. 2012;16;117–123.

13. Balarak D, Mostafapour FK, Joghataei A. Adsorption of Acid Blue 225 dye by Multi Walled Carbon Nanotubes: Determination of equilibrium and kinetics parameters. Der Pharma Chemica, 2016, 8(8):138-145.

14. Yang Y, Wei B, Zhao Y, Wang J. Construction of an integrated enzyme system consisting azoreductase and glucose 1-dehydrogenase for dye removal.Bioresource Technology. 2013;130; 517–521.

15. Couto SR. Dye removal by immobilised fungi.Biotechnology Advances; 2009. 27; 227–235.

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

17. Zazouli MA, Balarak D, Mahdavi Y. Effect of Azolla filiculoides on removal of reactive red 198 in aqueous solution. J Adv Environ Health Res. 2013; 1(1):1-7.

18. Oei BC, Ibrahim S, Wang S, Ang HM. Surfactant modified barley straw for removal of acid and reactive dyes from aqueous solution.Bioresource Technology. 2009.100; 4292–4295.

19. Demirbas A. Agricultural based activated carbons for the removal of dyes from aqueous solutions: A review.Journal of Hazardous Materials; 2009.167;1–9.

20. Safa Y, Bhatti HN. Adsorptive removal of direct textile dyes by low cost agricultural waste: Application of factorial design analysis.Chemical Engineering Journal. 2011;167;35-41.

21. Mahmoodi NM, Arami M, Bahrami H, Khorramfar S. Novel biosorbent (Canola hull): Surface characterization and dye removal ability at different cationic dye concentrations. Desalination. 2010. 264; 134–142.

22. Robinson T. Chandran B. Nigam P. Removal of dyes from an artificial textile dye effluent by two agricultural waste residues, corncob and barley husk. Environment International. 2002; 28(1-2);29–33.

23. Ferdag C, Necip AO. Biosorption of acidic dyes from aqueous solution by Paenibacillus macerans: Kinetic, thermodynamic and equilibrium studies. Chemical Engineering Journal. 2009;150(1):122-30.

24. Lu C, Chiu, H. Adsorption of zinc(II) from water with purified carbon nanotubes. Chemical Engineering Science. 2006; 61, 1138–1145.

25. Li Y-H, Wang S, Luan Z, Ding J, Xu C, Wu D. Adsorption of cadmium(II) from aqueous solution by surface oxidized carbon nanotubes. Carbon.2003. 41, 1057-62.

26. Kabbashi NA, Atieh MA, Al-Mamun A, Mirghami ME. Kinetic adsorption of application of carbon nanotubes for Pb(II) removal from aqueous solution. J. Environ. Sci. 2009. 21, 539–44.

27. Balarak D, Mahdavi Y, Bazrafshan E, Mahvi AH, Esfandyari Y. Adsorption of fluoride from aqueous solutions by carbon nanotubes: determination of equilibrium, kinetic, and thermodynamic parameters. Fluoride. 2016; 49(1)71-83.

28. Balarak D, Mahdavi Y and Mostafapour FK. Application of Alumina-coated Carbon Nanotubes in Removal of Tetracycline from Aqueous Solution. British Journal of Pharmaceutical Research.2016; 12(1): 1-11.

29. Balarak D, Mahdavi Y, Maleki A, Daraei H and Sadeghi S. Studies on the Removal of Amoxicillin by Single Walled Carbon Nanotubes. British Journal of Pharmaceutical Research. 2016;10(4): 1-9.

30. Balarak D, Azarpira H,. Rice husk as a Biosorbent for Antibiotic Metronidazole Removal: Isotherm Studies and Model validation. International Journal of ChemTech Research. 2016; 9(7); 566-573.

31. Balarak D, Mostafapour FK. Canola Residual as a Biosorbent for Antibiotic Metronidazole Removal. The Pharmaceutical and Chemical Journal, 2016, 3(2):12-17.

32. Tilaki RA, Yousefi Z, Charati JY, Balarak D. Comparison of Modified Canola and Azolla Efficiencies in Phenol Adsorption from Aqueous Solutions: An Adsorption Isotherm and Kinetics Study. Journal of Health and Development. 2014.3(3); 231-244.

33. Balarak D, Mostafapour FK, Joghataei A. Adsorption of Acid Blue 225 dye by Multi Walled Carbon Nanotubes: Determination of equilibrium and kinetics parameters. Der Pharma Chemica, 2016, 8(8):138-145.

34. Malakootian M, Balarak D, Mahdavi Y, Sadeghi SH, Amirmahani N. Removal of antibiotics from wastewater by azolla filiculoides: kinetic and equilibrium studies. International Journal of Analytical, Pharmaceutical and Biomedical Sciences. 2015;4(7);105-113

35. Gök O, Özcan S, Özcan A. Adsorption behavior of a textile dye of Reactive Blue 19 from aqueous solutions onto modified bentonite. Journal of Hazardous Materials. 2007;140(1-2);173-179.

36. Chandrasekhar S, Pramada PN. Rice husk ash as an adsorbent for methylene blue-effect of ashing temperature. Adsorption; 2006;12, 27–43.

37. Balarak D, Bazrafshan E, Kord Mostafapour F. Equilibrium, Kinetic Studies on the Adsorption of Acid Green 3(AG3) Dye Onto Azolla filiculoides as Adosorbent. American Chemical Science Journal.2016;11(1);1-10.

38. Balarak D. Kinetics, Isotherm and Thermodynamics Studies on Bisphenol A Adsorption using Barley husk. International Journal of ChemTech Research. 2016;9(5);681-90.

39. Low KS, Lee CK, Tan BF. Quaternized wood as sorbent for reactive dyes. Applied Biochemistry and Biotechnology. 2000; 87, 233–245.

40. Zeroual Y, Kim BS, Kim CS, Blaghen M, Lee KM. Biosorption of bromophenol blue from aqueous solutions by Rhizopus stolonifer biomass. Water Air and Soil Pollution. 2006; 177, 135–146.

41. Mane VS ,Mall ID. Kinetic and equilibrium isotherm studies for the adsorptive removal of Brilliant Green dye from aqueous solution by rice husk ash, J. Environ. Manage.2007: 84 ;390–400.

42. Balarak D, Azarpira H, Mostafapour FK. Thermodynamics of removal of cadmium by adsorption on Barley husk biomass. Der Pharma Chemica, 2016,8(10):243-47.

43. Hao Chena H, Bin Gaoa B, Lib H. Removal of sulfamethoxazole and ciprofloxacin from aqueous solutions by graphene oxide. Journal of Hazardous Materials.2015;283;201-07.

44. Padmesh TVN, Vijayaraghavan K, Sekaran G, Velan M. Batch and column studies on biosorption of acid dyes on fresh water macro alga Azolla filiculoides. J Hazardous Mat. 2005; 4(125):121-9.

45. Crini G, Peindy HN, Gimbert F, Robert C. Removal of C.I. Basic Green 4 (Malachite Green) from aqueous solutions by adsorption using cyclodextrin-based adsorbent: Kinetic and equilibrium studies. Separation and Purification Technology. 2007;53;97-110.

46. Peng H, Pana B, Wu M, Ran Liu R, Zhanga D, Wu D, Xing B. Adsorption of ofloxacin on carbon nanotubes: Solubility, pH and cosolvent effects. Journal of Hazardous Materials. 2012;211-212;342-48.

47. Ali I. The quest for active carbon adsorbent substitutes: Inexpensive adsorbents for toxic metal ions removal from wastewater. Sepn. & Purfn. Rev. 2010;39(3-4):91-171.

48. Tor A, Cengeloglu Y. Removal of congo red from aqueous solution by adsorption onto acid activated red mud. Journal of Hazardous Materials. 2006;138(2):409-15.

49. Low KS, Lee CK, Tan BF. Quaternized wood as sorbent for reactive dyes. Biochem Biotechnol. 2000;87:233-45.