The application of Azolla filiculoides biomass in acid blue 15 dye (AB15) removal from aqueous solutions

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Abstract

Introduction: Industrial wastewater is one of the most important environmental pollutants. Discharging the colorful industrial effluents into receiving waters can lead to eutrification which has many adverse effects on human health. Therefore, the present study aimed at evaluatingacid blue 15 dye removal from aqueous solution by dried Azolla.
Materials and methods: Azolla biomass was dried in the sunlight, and then crushed and sieved to particle sizes in range of 1-2 mm. Next, it was treated with 0.1 M HCl for a period of 5 hours. The Azolla was washed with distilled water and used as absorbent. The effect of operating parameters such as pH, contact time, AB 15 concentration and adsorbent dose on the AB15 removal efficiency was investigated. The dye concentration was measured by spectrophotometer (DR4000) at λmax =565nm.
Results: In optimum condition (pH 3, contact time 90 min , absorbent dose 10 g/l and AB15 concentration 10 ppm), application of Azolla removed 98% of AB15 from aqueous solutions. The equilibrium data was best fitted on Langmuir isotherm and the adsorption kinetic model followed a pseudo-second model.
Conclusion: The obtained results showed that the dried Azolla can be used as a high efficiency and low-cost absorbent to treat textile effluents.

Keywords: Azolla filiculoides, AB15 dye, isotherm's model, adsorption, water treatment

Introduction

Synthetic dye is one of the most serious problems for environment because it may become toxic due to decomposition (1, 2). The amount of generated dye is estimated in the range of 7×105-106 ton/year which is used in many industries such as production of cosmetic, leather, paper and textile (3-5). Maximum dye consumption is used in textile industry and these industries can produce high volume wastewater with dye concentration in the range of 10-200 mg/l(3, 6). Approximately, 10-20% of total world production of dyes is lost during the painting process and is released into wastewater streams (7, 8). The dyes are formed with different chemical structures such as acidic,

basic, reactive, disperse, azo, anthraquinone and metal dyes (9, 10). Discharging the wastewaters into receiving waters leads to eutrification and interference in the ecology (11). Most dyes have carcinogenic and mutagenic properties and can cause allergy and dermatitis (11). Various methods were used to treat the textile effluents such as biological, membrane process, advanced oxidation process, etc. (12-14). Most conducted studies on dye removal are based on advanced oxidation process; however, the formation of by-product and their high cost is considered as a major problem (9). Adsorption process is one of the most common processes used in water and wastewater treatment (15, 16). Typically, adsorption process is performed by activated carbon. Although the advantages of activated carbon are the high capacity and adsorption surface, it is expensive and requires expertise (17, 18). Therefore, researchers have attempted to use the natural and low cost adsorbents instead of commercial carbon (11, 18, 19). Nowadays, different natural adsorbents such as chitosan, fly ash, peach kernel, olive, charcoal, barley and wheat straw, sawdust are used to remove organic and inorganic pollutants (11, 18, 20-22). A number of studies suggest the using of biosorption methods such as plant biomass to treat these wastewaters (23). Azolla is a flouting aquatic fern which has a rapid growing rate in stagnant waters and wetlands and can rapidly cover the surface of water (24, 25). Therefore, it can be a serious problem for aquatic life and many studies are conducted to eliminate this plant in the Anzali wetlands. Dried Azolla is used as high efficiency and inexpensive adsorbent to remove the organic substances such as dyes and heavy metal in many countries of the world due to its adsorbing properties. Table 1 shows the sorption capacity for Azolla adsorbent used to remove pollutants (26-31). Therefore, the purpose of this study was to use dried Azolla as an effective and low cost adsorbent to remove reactive Acid Blue15 from aqueous solutions.

Table 1. The removal efficiency of pollutant by using the Azolla.

Author	Pollutant	Removal efficiency
Balarak D	Pyrocatechol	97%
Balarak D	Phenol	99%
Padmesh TVN	Acid red 88, acid green 3, acid orange 7	99%
Pandey VC	Heavy metals	96%

Material and method

Adsorbent preparation: Azollafiliculoides was collected from rice fields of Sari. It was sun dried then crushed and finally sieved to particle sizes in the range of 1–2 mm. The biomass was treated with 0.1 M HCl for 5 h followed by washing with distilled water and then dried in shade (32). The resultant biomass was subsequently used in absorption experiments. The specific surface area of adsorbent was determined by the BET method using the Gemini2357 of micrometrics Co. Scanning electron microscopy (SEM) of the modified Azollafiliculoides were carried out using Philips, Eindhoven.

Materials: The AB15 dye was supplied from Alvansabet Co. the stock solution (1000mg/l) was prepared and desired concentration of dye solution was prepared by dilution of stock solution. The General characteristics and chemical structures of AB15 are presented in Table 2 and Figure 1, respectively.

Table 2. Properties of AB15(33).

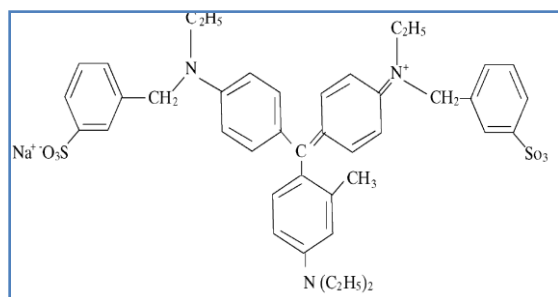| C.I. name	Molecular weight	λmax (nm)	Molecular formula
Acid Blue15	775.96	565	$C_{42}H_{46}N_3NaO_6S_2$

Figure 1. The chemical structures of AB15 (33).

Batch adsorption experiments: The literature review indicated that the most important effective variables on adsorption are pH, adsorbent dose, contact time, and pollutants concentrations. Therefore, the initial AB15 concentration was selected (10-200 mg/l). The effect of absorbent dosage (0.2-1.4 g/100 ml), contact time (10 - 180 min) and pH (3- 11) were investigated. The experiments in batch system were carried out using 100ml in a 250 ml Erlenmeyer flask Meyer. In each adsorption experiment, certain concentration of AB15 solution was added into the flask. In every experiment, a certain concentration of AB15 and specific dose of absorbent poured into the Flask and completely mixed with magnetic stirrer at 3600 rpm for 60 minutes. Then, the sample was centrifuged at 3600 rpm for 10 minutes. Finally, the residual concentrations were measured using spectrophotometer at λmax of 565 nm (33). The amount of adsorbed AB15 was calculated according to the following Eq 1(34).

$$q_e = (C_O - C_e)\ V/m \quad \text{Eq1}$$

Where qe is the amount of adsorbed (mg/g), C_0 and C_e are the initial and equilibrium concentrations of liquid phase (mg/L),

respectively. V is the volume of the solution (L), and m is the mass of the adsorbent (g).

Adsorption isotherms: The equilibrium adsorption isotherm is an important parameter for the design of adsorption systems. Although several isotherm equations are available, two important isotherms of Langmuir and Freundlich isotherms were selected. The Langmuir isotherm is presented in the Eq2 (34, 35).

$$Ce\ /\ q_e = 1/q_m\ K_L + Ce\ /\ q_m \quad \text{Eq2}$$

Where qe is the amount of sorbatebiosorbed at equilibrium (mg/g); C_e is the equilibrium concentration of the sorbate or the sorbateunadsorbed in the solution (mg/L); q_m (mg/g) is the maximum theoretical biosorption capacity and K_L (L/mg) is a measure of biosorption energy that is indicated on the affinity between biosorbent and sorbate.

The Freundlich equation is given by the following Eq3 (36, 37):

$$Log\ x/m = 1/n\ log\ Ce + log\ KF \quad \text{Eq3}$$

Where q_e is the sorbatebiosorbed at the equilibrium (mg/g); C_e is the equilibriumconcentration of the sorbate or the unabsorbed sorbate in the solution (mg/L); K_F is a constant, indicative of biosorptioncapacity(36). Table 2 shows the Freundlich and Langmuir equation obtained for the biosorption of AB15 onto dried A. filiculoides.

Adsorption kinetics: Kinetic models are used to examine the rate of the adsorption process and potential rate controlling step. In the present study, obtained kinetic data were analyzed from batch studies using the pseudo second-order and pseudo First-order model.

The pseudo-first-order rate equation is expressed as Eq 4 (38):

$$log\ (q_e - q) = log\ q_e - k_1 t\ /\ 2.3 \quad \text{Eq4}$$

Where q_e and q are the amounts of AB15 adsorbed (mg/g) at equilibrium and at time t (min), respectively, k1 is the rate constant of adsorption (min^{-1}). Values of k_1 were calculated from the plots of log (q_e-q) versus (t) for different concentrations.

Also, equation 5 provides the pseudo-second-order rate equation:

$$dq / dt = k_2 (q_e - q)^2 \quad Eq5$$

Where K_2 is the second order rate constant (g mg −1min−1), q and qe are the amount of the adsorbed on the adsorbent (mg/g) at equilibrium and at time t. The integration fromEq 6is as follows:

$$t/q = 1/k2qe2 + 1/ qet \quad Eq6$$

If the second-order kinetic equation is applicable, the plot of t/q against t of Eq (6) will give a linear relationship. The qe and K2 can be determined from the slope and the intercept of the plot.

Results

Scanning electron microscopy (SEM) images were used to analyze the surface structure of A. Filiculoides (Fig. 2). It was found that the adsorbent has Heterogeneous surface structure with deep pores. The specific surface area of modified Azolla was determined in the size of 36 m^2/g.
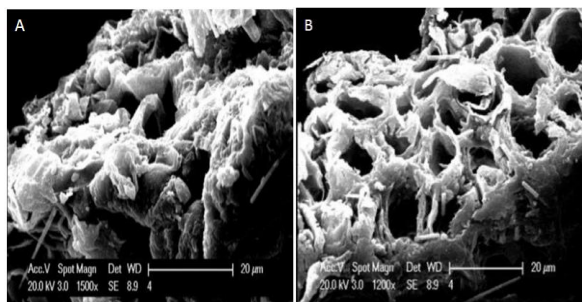

Figure 2. SEM photographs of adsorbent: (A) before use,(B) after use.

The effect of contact time and initial dye concentration: Increasing the contact time raised the adsorption percentage; however, adsorption ratio reached equilibrium after 90 min. The dye removal efficiency was decreased by increasing initial concentration. Figure 3 presents the effect of contact time and initial dye concentration on dye removal. As can be observed,in dye concentration of 200 and 10 mg/l, the dye removal efficiency is 49 and 98%, respectively.
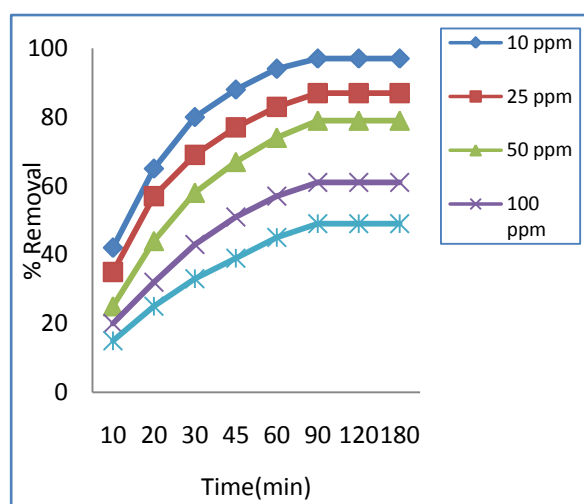

Figure 3. Effect of contact time and initial dye concentration on removal efficiency (pH = 3, adsorbent dosage 1 g/100cc).

The effect of pH and adsorbent dosage: Figures 3, 4 and 5 shows the effect of pH and adsorbent dosage on adsorption rate. As it is seen, the maximum adsorption rate was performed in acidic pH and it is decreased in alkaline pH. The adsorption rate was raised by increasing the adsorbent dosage up to the concentration of 10 g/L, and then reached to equilibrium. As a result, adsorption rate was also enhanced by increasing the adsorbent dosage.

Adsorption kinetics and isotherms: Table 2 and 3 show the isothermal models and adsorption kinetics.
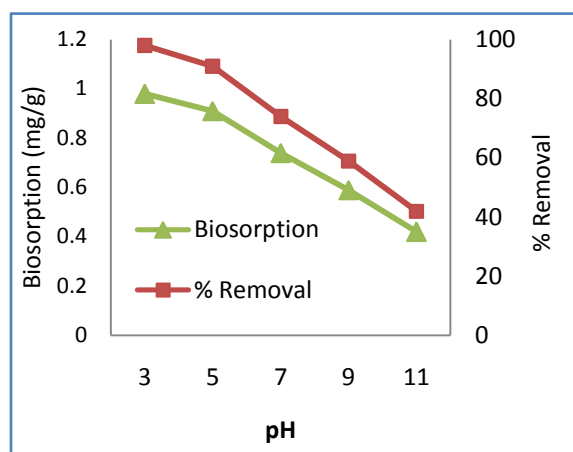
Figure 4. Effect of pH on removal efficiency of AB15 (contact time = 90min, dose: 10g/l, AB15 concentration: 10ppm).
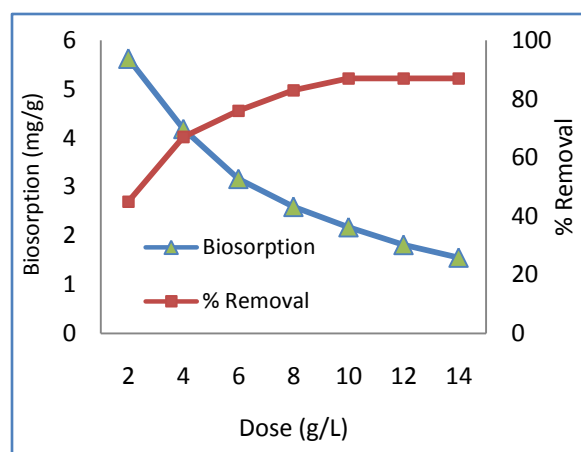

Figure 5. Effect of adsorbent dose on removal efficiency of AB15 (contact time = 90 min, PH = 3, AB15 concentration: 25 ppm).

Table 3. The isotherms constants for the removal AB15 dye.

Langmuir model			Freundlich model		
b(ml/g)	R^2	q_m	K_F	R^2	1/n
1.11	0.998	7.1	51.2	0.963	1.02

Table 4. The kinetic model constants for the removal AB15 at 10, 25, 50 mg/L dye concentrations

co(mg/L)	Pseudo second-order model			Pseudo First-order model		
	K_2(g/mg min)	R^2	q(mg/g)	k_1(1/ min)	R^2	q(mg/g)
10	0.07	0.988	1.84	0.060	0.948	1.45
25	0.10	0.992	3.90	0.075	0.964	3.40
50	0.114	0.998	5.90	0.088	0.978	5.60

Discussion

The specific surface area is related to the number of active adsorption sites of dried A. filiculoides.The adsorption was increased with the specific surface area and pore volume of the sorbent. The specific surface area of themodified Azolla was determined in the size of 36 m²/g. This situation indicated that the modified Azolla has a

relatively good ability to remove the pollutants (9).
With regard to the present study, the dye removal efficiency enhances by increasing contact time which is due to more contact between pollutant and adsorbent. The dye adsorption was rapidly performed in initial minutes of the sorption process. Adsorption rate decreases with time which can decline

the dye concentration and lower active points on adsorbent surface area. There are a lot of empty spaces in the early stages of adsorption and they were occupied by dye molecules with time. This situation is consistent with several studies that were conducted on dye removal by Azolla (29, 39).

The greater adsorption occurs in low concentrations and dye removal efficiency reduces with increasing initial concentration of dye. Since the adsorbents have little adsorption sites, their adsorption capacity is therefore saturated by increasing the pollutant concentration and the removal efficiency will reduce.

The results of this study are in line with previous studies (30, 36). pH plays an important role in all processes and adsorption capacity. It can influence various aspects of adsorption including adsorbent surface charge, the degree of ionization, and separation of functional groups on the active sites of adsorbent and solution chemistry. Many researchers have reported that pH plays a main role in electrostatic force between adsorbent and AB15. In this study, the maximum AB15 removal was obtained in pH=3 which is similar to previous studies on dye removal by azolla. This is probably due to the binding group between adsorbent and adsorbate (9, 29).The adsorption rate enhances by an increase in adsorbent dose which is due to increasing the active surface of adsorbent. The results show that although efficiency rises with increasing adsorbent dose, the dye adsorbed per gram of adsorbent decreases and active sites of adsorbent are not saturated because of it. So,

when the adsorbent dose increases, the total capacity of the adsorbent surface points is not completely used and this reduces the adsorption rate per unit mass of the adsorbent (3, 12).

The Freundlich equation is based on the hypothesis of multi-layer biosorption and the linear form is given by the following equation and Langmuir isotherm assumes monolayer coverage of a sorbent on the solid surface of adsorbent, uniform energy of sorption, and no transmigration of sorbate in the surface of plant. The obtained equilibrium data from AB15 adsorption by this plant indicated that the data is better fitted on Langmuier isotherm (R2=0.998) than Freundlich isotherm (R2=0.963) which is in line with the studies that are performed by this plant for dye removal (6, 28, 30). Kinetics of adsorption was well described by pseudo-second order model. The result of this study is consistent with other studies(19, 29, 32).

Conclusion

According to the obtained results, Azolla can be used as an effective, inexpensive, and available adsorbent to treat the effluents with organic compound (dye) such as textile wastewater. The dye removal efficiency depends on various parameters such as contact time, pH, adsorbent dose, and initial dye concentration.

Acknowledgement

References

1. KhorramfarS, Mahmoodi NM, Arami M, Gharanjig K. Dye removal from colored textile wastewater using tamarindusindica hull: adsorption isotherm and kinetics study. DyeSci Technol. 2012;3(1):81-8.
2. GokO, Ozcan AS, Ozcan A. Adsorption behavior of a textile dye of Reactive

Blue 19 from aqueous solutions onto modified bentonite. Appl Surf Sci. 2010; 256 (17):5439-43.

3. Zazouli MA, Yazdani J, Balarak D, Ebrahimi M, Mahdavi Y. Removal Acid Blue 113 from Aqueous Solution by Canola. J Mazandaran Uni Med Sci. 2013; 23(2):73-81.

4. Yazdanbakhsh AR, Mohammadi AS, Sardar M, Mohammadi H, Zarabi M. Investigation of Iron Powder, Hydrogen Peroxide and Iron Hydrogen Peroxide for Removal of Acid Yellow Powder 36 Dye from Aqueous Solutions. Health Environ. 2010; 2(4):295-302.

5. Samarghandi MR, Sepehr MN, Zarrabi M, Norouzi M. Mechanism and Removal Efficiency of C.I. Acid Blake 1 by Pumice Stone Adsorbent. Health Environ. 2011; 3(4):399-410.

6. Patil AK, Shrivastava VS. Alternantherabettzichiana plant powder as low cost adsorbent for removal of Congo red from aqueous solution. International journal of chemistry technology resources. J Health. 2010; 9(2):842–50.

7. Lin L, Zhai S-R, Xiao Z-Y, Song Y. Dye adsorption of mesoporous activated carbons produced from NaOH-pretreated rice husks. Bioresource Technol. 2013; 10(136):437–43.

8. Mahvi A, Heibati B. Removal efficiency of azo dyes from textile effluent using activated carbon made from walnut wood and determination of isotherms of acid red18. Public Health J. 2009; 1(3):7-15.

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

10. Tan L, Ning S, Xia H, Sun J. Aerobic decolorization and mineralization of azo dyes by a microbial community in the absence of an external carbon source. Int Biodeterior Biodegrad. 2013:7(85):210-6.

11. Zazouli MA, Balarak D, Mahdavi Y, Ebrahimi M. Adsorption rate of 198 reactive red dyes from aqueous solutions by using activated red mud. Iran J Health Sci. 2013; 1(1):29-40.

12. Safa Y, Bhatti HN. Adsorptive removal of direct textile dyes by low cost agricultural waste: Application of factorial design analysis. Chem Engin J. 2011; 12(167):35–41.

13. Naddafi K, NabizadehNodehi R, Jahangiri Rad M. Removal of Reactive Blue 29 Dye from Water by Single-Wall Carbon Nanotubes. Iran J Health Environ. 2011; 3(4): 359-68.

14. Shokouhi R, Hosseinzadeh E, Zare M, Torabi E. Sodium Alginate Magnetic Beads for Removal of Acid Cyanine 5R from aqueous solution. Hormozgan Med J. 2011;1(2):101-11.

15. 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.

16. Shokohi R, Jafari Z. removal dye Acid Blue 113 from aqueous environment by adsorption on Activated red mud. J Med Kordestan. 2011; 16(4):55-65.

17. Garg VK, Renuka G, AnuBala Y, Rakesh K, Dye removal from aqueous solution by adsorption on treated sawdust, Bioresour. Technology. 2003; 89(3):121-7.

18. Toor M, Jin B. Adsorption characteristics, isotherm, kinetics, and diffusion of modified natural bentonite for removing diazo dye. Chem Engin. 2011; 6(187):79-88.

19. Ponnusami V, Krithika V, Madhuram R, Srivastava SN. Biosorption of reactive dye using acid-treated rice husk: Factorial design analysis. J Hazardous Mat. 2007; 8(142):397–403.

20. Crini G, Badot PM. Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature. Prog Polymer Sci. 2008; 33(4):399-447.
21. Oladoja NA, Aboluwoye CO, Oladineji YB. Studies on castor seed shell as a sorbent in basic dye contaminated wastewater remediation. Desalination. 2008; 14(227):190-203.
22. Wang S, Boyjoo Y, Choueib A, Zhu ZH. Removal of dyes from aqueous solution using fly ash and red mud. Water Res. 2005; 39:129-38.
23. Dianati RA, Yazdani J, Belarak D. Effect of sorbitol on phenol removal rate by lemna minor. Mazandaran Uni Med Sci. 2013; 22(2):58-64.
24. Jain SK, Gujral GS, Jha NK, Vasudevan P. Production of biogas from Azollapinnata R.Br and Lemna minor L.: Effect of heavy metal contamination. Bioresource Technol. 1992; 41(3):273-7.
25. Filizade Y. Survey Ecology Excessive Growth Of Azolla In Anzali Wetland And Quality Control. Iran Nat Resources. 2003; 55(1):65-82.
26. Zazouli MA, Balarak D, Mahdavi Y. Pyrocatechol Removal from Aqueous Solutions by Using Azolla filiculoides. Health Scope. 2013; 2(1):1-6.
27. Diyanati RA, Yousefi Z, Cherati JY, Balarak D. Adsorption of phenol by modified azolla from Aqueous Solution. J Mazandaran Uni Med Sci. 2013; 22(2):13-21.
28. Diyanati RA, Yousefi Z, Cherati JY, Balarak D. The ability of Azolla and lemna minor biomass for adsorption of phenol from aqueous solutions. J Mazandaran Uni Med Sci. 2013; 23(106).17-23.
29. Padmesh TVN, Vijayaraghavan K, Sekaran G, Velan M. Application of Azollarongpong on biosorption of acid red 88, acid green 3, acid orange 7 from synthetic solutions. Chem Engin J. 2006; 11(122):55-63.
30. Tan C-y, Li M, Lin Y-M, Lu X-Q, Chen Z-l. Biosorption of Basic Orange from aqueous solution onto dried A. filiculoides biomass: Equilibrium, kinetic and FTIR studies. Desalination. 2011:266(1-3):56-62.
31. Pandey VC. Phytoremediation of heavy metals from fly ash pond by Azollacaroliniana. Ecotoxicol Environ Safety. 2012:82(2):8-12.
32. Padmesh TVN, Vijayaraghavan K, Sekaran G, Velan M. Batch and column studies on biosorption of acid dyes on fresh water macro alga Azollafiliculoides. J Hazardous Mat. 2005; 4(125):121-9.
33. Samanjit A, Walia TPS, Ravneet K. Removal of health hazards cuasing acidic dyes from aqueous solution by the process of adsorption. J Health Allied Sci. 2007; 6(3):14-21.
34. Zazouli MA, Balarak D, Mahdavi Y, Barafrashtehpour M, Ebrahimi M. Adsorption of bisphenol from industrial wastewater by modified red Mud. J Health Develop. 2013; 2(1):1-11.
35. Dogan M, Abak H, Alkan M. Biosorption of Methylene Blue from Aqueous Solutions by Hazelnut Shells: Equilibrium, Parameters and Isotherms. Water Air Soil Poll. 2008; 192(1-4):141-53.
36. Zazouli MA, Balarak D, Mahdavi Y. Application of azollafiliculoides biomass for 2-Chlorophenol and 4-Chrorophenol Removal from aqueous solutions. Iran J Health Sci. 2013; 1(2):20-30.
37. Nateghi R, Bonyadinejad GR, Amin MM. Nickel oxide nanoparticles application as an efficient adsorbent for dye removal from synthetic wastewater treatment. Health Sys Res. 2009; 6:1015-21.

38. Zazouli MA, Balarak D, Karimnejhad F. Kinetics modeling and isotherms for adsorption of fluoride from aqueous solution by modified lemna minor. J Mazandaran Uni Med Sci. 2013; 23(107):31-39.

39. Vafaei F, Khataee AR, Movafeghi A, SalehiLisar SY, Zarei M. Bioremoval of an azo dye by Azollafiliculoides: Study of growth, photosynthetic pigments and antioxidant enzymes status. Int Biodeter Amp Biodegrad. 2012:75:194-200.