

Original Research Article

Adsorption Properties of Thermally Treated Rice Husk for Removal of Sulfamethazine Antibiotic from Pharmaceutical Wastewater

ABSTRACT

Aim: this study aims to demonstrate the adsorption properties of thermally treated rice husk for removal of sulfamethazine (SMT) antibiotic from pharmaceutical wastewater.

Methodology: Rice husk was treated thermally and then it was put in a desiccator for cooling and after that it was kept in a container for the adsorption experiments. The adsorption tests were carried out by using batch experiments.

Results: Of the three adsorption isotherm, the R^2 value of Langmuir isotherm model was the highest. Also compared to other isotherms, the AARE coefficient for the Langmuir isotherm is low, which indicates favorable sorption. The mean free energy was estimated from Dubinin–Radushkevich isotherm model to be 9.18 KJ/mol which clearly proved that the adsorption experiment followed a physical process.

Conclusion: It could be concluded that rice husk that is modified with thermally process is a potential and active bio sorbent for removal of SMT from its aqueous solution and industrial waste water remediation.

Keywords: AARE, isotherm model, sulfonamide antibiotics, thermally treated rice husk

1. INTRODUCTION

In recent years, increasing awareness of water pollution and its far reaching ~~effects-effects~~ has prompted concerted ~~efforts-efforts~~ towards pollution abatement [1-3]. Pharmaceuticals constitute a large group of human and veterinary medicinal compounds which have long been used throughout the world [4, 5]. The most important pharmaceuticals found in the waters are antibiotics, analgesics, painkillers, and hormonal drugs [6]. These chemicals find their way into the water via sewage systems of drug manufacturing plants, hospitals, and private households [7,8]. Generally, the amount of pharmaceuticals in the aquatic environment is low [9]. Antibiotics are widely used as effective clinical pharmaceuticals to prevent and treat diseases, and they are mainly excreted into the aquatic and soil environments in unchanged and active forms [10, 11].

Therefore, over the past few years these compounds are considered to be an emerging environmental problem. Pharmaceuticals are released to the environment through many ways, including municipal medical and industrial wastewater effluents [12, 13]. They are extremely resistant to biological degradation processes and because of their continuous discharge, they remain in the environment for a long time; their presence in the environment has caused increased concern over long-term effect on human health [14, 15]. Therefore, the removal of pharmaceuticals before disposal of the wastewater is necessary.

Conventional metal removal techniques such as ion exchange, precipitation, membrane separation, electrochemical precipitation–filtration and reduction followed by chemical precipitation are often expensive or not sufficiently effective in the low concentration range [16, 17]. Adsorption is one of the important procedures for the removal of trace antibiotics from aqueous solution. The main properties of the adsorbents for antibiotics removal are strong affinity and high loading capacity [18, 19]. Hence, low cost adsorbents with high metal binding affinity need to be investigated. Waste materials from agricultural and food industries used as adsorbents have the dual advantage of waste reuse and low cost [20].

Rice husks are usually used as a low-value energy resource, burned in the field, or discarded, which are unfavorable to environment. The processing and transformation of rice husks with good adsorption properties would alleviate problems of disposal and management of these waste by-products, while producing value added

products from rice husks for water and wastewater treatment, etc., to expand the cheap materials market to adsorption pollutants [21, 22].

In the present study, we have prepared a novel adsorbent with thermally process and this new adsorbent was used for removal of Sulfamethazine (SMT) from aqueous solutions. Adsorption isotherms on the adsorption of SMT were studied in a batch system. The effects of the SMT concentration, temperature and contact time were studied to determine the optimal adsorption conditions.

2. METHODOLOGY

2.1. Materials

All chemicals used in this work were of GR grade and was obtained from Sigma Aldrich (Darmstadt, Germany). The chemical structure of SMT antibiotics (molecular weight: 278.33, EC Number 200-346-4 and CAS Number 57-68-1 and Molecular Formula $C_{12}H_{14}N_4O_2S$) is shown in Fig. 1. The pH of the solution was adjusted by 0.1 M H_2SO_4 or NaOH (model Sartorius Professional Meter PP-50). All experiments were conducted in batch mode in 250 mL conical flasks.

2.2. Preparation of sorbent

Rice husk collected from a local rice mill was grounded and washed with ultrapure water several times to eliminate impurities and to obtain constant pH before dried in an oven at $105^\circ C$ for 24 h. The dried rice husk was sieved to obtain particles size between 300 to 600 μm and then it was heated in a furnace at $800^\circ C$ for two hours. The thermally treated rice husk was then put in a desiccator for cooling before keeping it in a container for the adsorption experiments.

2.3. Adsorption study: Adsorption tests were carried out by using batch experiments. For each test, 2 g of the adsorbent was placed in screw-capped Erlenmeyer flasks containing 100 mL of MG solution. The flasks were shaken constantly for a sufficient period to achieve equilibrium using an orbital shaker at 180 rpm and $28^\circ C$. Then the solution was filtered using Whatman filter paper. The dye uptake was monitored with a spectrophotometer by maximum wave length of 290 nm. The adsorption at the equilibrium, q_e (mol/g), was calculated using the following equation (23, 24):

$$q_e = (C_0 - C_e) \frac{V}{M}$$

At first mention, give the full :[1A]Comment name, then abbreviation in bracket

Which specification?, number :[2A]Comment

Using literature value is not :[3A]Comment always advisable, since it varies with temperature, hence better you determine it experimentally

Where C_0 and C_e (mol/L) are the initial and the equilibrium liquid-phase concentrations of the dye, respectively. V is the volume of the solution (in liters), and m is the mass of the dry adsorbent (in grams). The equilibrium adsorption data were fitted with three isotherm models, the Langmuir and Freundlich and Dubinin-Radushkevich models.

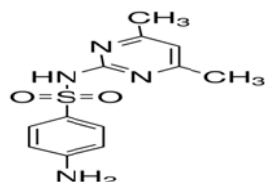


Fig.1. Molecular structure of Sulfamethazine (SMT)

3. RESULTS AND DISCUSSION

3.1. Adsorption isotherm

For the analysis of equilibrium data for SMT adsorption onto the TTRH, Langmuir isotherm model and Freundlich isotherm model were used. Langmuir isotherm model is assumed monolayer adsorption onto surface with a finite number of identical sites (25, 26). Linearity of the plots indicated the applicability of the adsorption isotherm. Weber expressed the essential characteristics and feasibility of the Langmuir isotherm in terms of a dimensionless constant, separation factor or equilibrium parameter, R_L . The linear form of the Langmuir adsorption isotherm and R_L constant can be defined by Eqs. 2 and 3. If this value ranges in between 0 and 1 then the adsorption process is favorable (27). All the experimental data were lying between 0 and 1 indicated favorable adsorption. The Freundlich isotherm is an empirical equation based on the adsorption on the heterogeneous surface (29, 30). The linear form of the Freundlich adsorption isotherm can be defined by Eq. 4. The Freundlich isotherm constant n was an empirical parameter that varies with the degree of heterogeneity and K_F was related to adsorption capacity. The constants K_F and n were calculated from Eq. 4 and Freundlich plots (Figs 2 b). Table 1 indicates the Langmuir and Freundlich constants along with the statistical parameters. The values of n lie between 1 and 10 represent favorable adsorption.

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K} \quad (2)$$

$$R_L = \frac{1}{1 + C_0 K} \quad (3)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)$$

3.2. Calculation of sorption energy

The Dubinin–Radushkevich isotherm model was used to predict the nature of adsorption process as physical or chemical by calculating sorption energy. The linear form of the model was described as (31, 32):

$$\ln C_{\text{abs}} = \ln X_m - \gamma \varepsilon^2$$

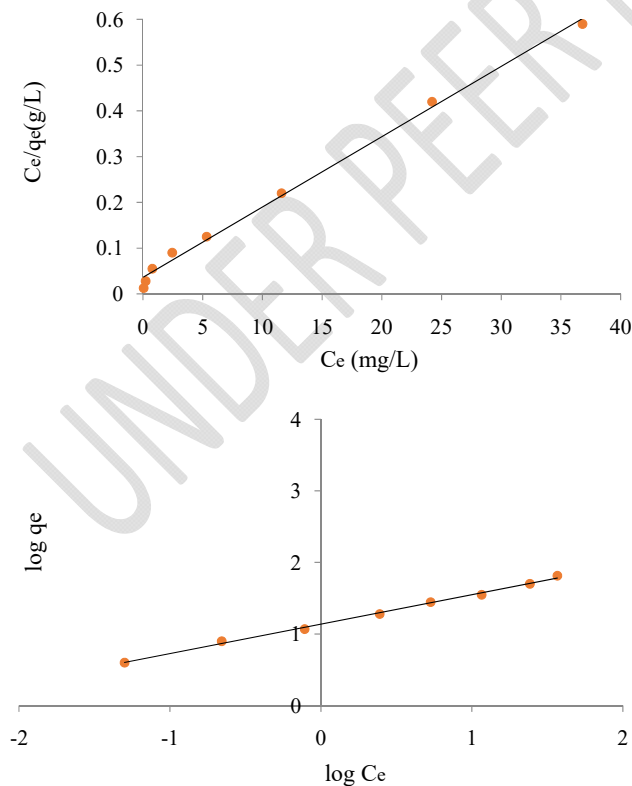
The Polanyi potential which is equal to (33, 34):

$$\varepsilon = RT + \ln \left(1 + \frac{1}{C_e} \right)$$

From Fig 2 C, a plot of $\ln C_{\text{abs}}$ versus ε^2 gave a straight line from which the values of γ and X_m for all the adsorbents were calculated. Using the value of γ , the mean sorption energy, E , was evaluated as (35, 36):

$$E = \frac{1}{\sqrt{-2\gamma}}$$

Provide the meaning of all the :[4A]Comment variables in the equations



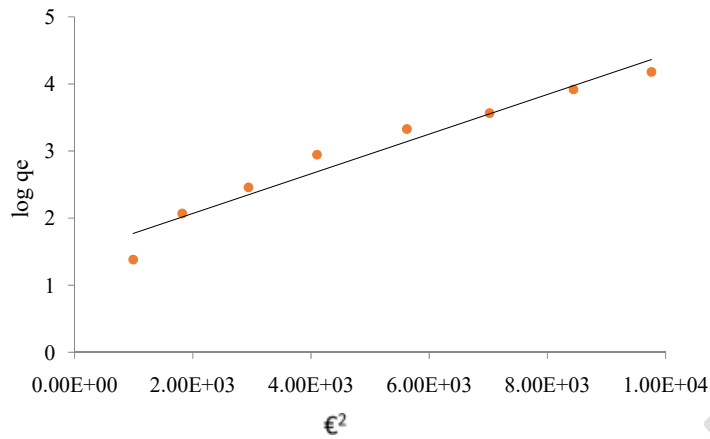


Fig.2. isotherm models for the adsorption of SMT adsorption onto TTRH, (a) Langmuir (b) Freundlich (c) Dubinin–Radushkevich

Give each figure its caption :[5A]Comment separately, i.e. Fig 2, Fig 3 etc

The Dubinin–Radushkevich isotherm relates the heterogeneity of energies close to the adsorbent surface. If a very small sub-region of the sorption surface was considered and assumed to be approximately by the Langmuir isotherm, the quantity $\sqrt{-\gamma}$ can be related to the mean sorption energy, E, which indicated the information about adsorption mechanism. If $E < 8$ kJ/mol, the adsorption process was physical in nature and in the ranges from 8 to 16 kJ/mol, it was chemical in nature. The estimated values of E are shown in Table 1 which suggested the adsorption process was chemical in nature.

Table 1: Langmuir, Freundlich and Dubinin–Radushkevich Isotherm constants for the adsorption of SMT by TTRH

Langmuir					Freundlich				Dubinin–Radushkevich				
q_m	AARE	K	R_L	R^2	n	AARE	K_F	R^2	q_m	AARE	Y	E	R^2
19.11	1.69	0.029	0.446	0.992	1.84	14.63	3.79	0.972	13.21	26.73	6.25	9.18	0.914

The average absolute value of relative error, AARE, was used to compare the predicted results with experimental data. This is defined as follows (37, 38):

$$\%AARE = \frac{1}{N} \sum_{i=1}^N \left(\frac{Pred\ value - Exp\ value}{Exp\ value} \right) \times 100$$

Which N is the number of data points. From Table 1, it can be concluded that the adsorption of SMT onto TTRH follow Langmuir adsorption isotherm model (according to high value of the R^2 coefficient or and the low value of the AARE coefficient).

3.3. Effect of temperature and contact time

The effect of temperature on the SMT adsorption onto TTRH was carried out at 10, 25, 40 and 55 °C and the results are illustrated in Fig. 3.

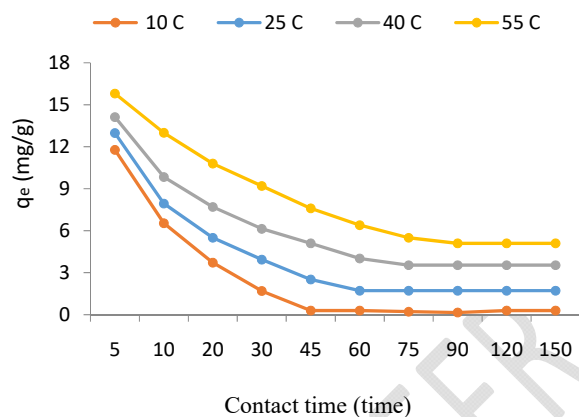


Fig 3. Effect of contact time and temperature on the removal of SMT by TTRH (concentration: 50 mg/L; dose: 2.5 g/L; shaking speed: 180 rpm; pH: 7)

An increase in the temperature led to an increase in the adsorption capacity, q_e , from 11.78 to 15.81 mg/g corresponding to a temperature change from 10 to 55 °C, indicating that SMT adsorption onto TTRH may be a kinetically controlled process. The higher temperature increases the reaction rate and decreases the particle density, which forms voids, resulting in a reduced equilibrium time (39, 40). The obtained result is consistent with observations ~~were~~ made by Ahmadi (10) on a study of the adsorption of antibiotics by nano-particle. The observed increase in the adsorption capacity with increasing temperature is a kinetic effect resulting from the increased monomer concentration in the solution.

Contact time is another important variable in adsorption processes. Fig. 4 shows the effect of contact time on adsorption for various SMT concentrations.

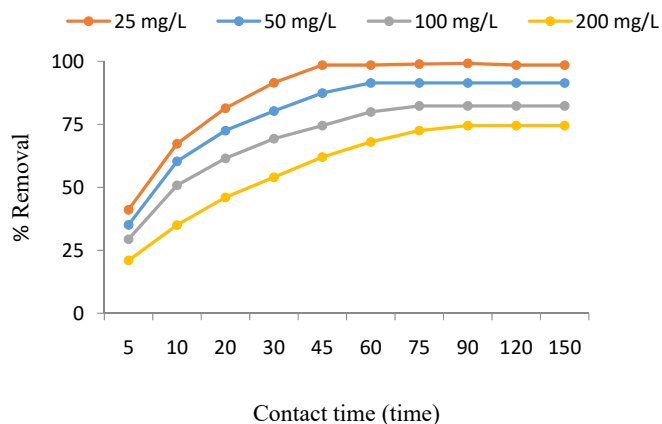


Fig 4. Effect of contact time and concentration on the removal of SMT by TTRH (Temp: 25°C; dose: 2.5 g/L; shaking speed: 180 rpm; pH: 7)

The results show that with increasing SMT concentration, the time required to reach equilibrium increased accordingly. For initial dye concentrations of 25, 50, 100 and 200 mg/L, the times reaching equilibrium were 45, 60, 75 and 90 min, respectively. At low initial concentrations, the SMT adsorption by TTRH was very intense and reached equilibrium very quickly. However, during the adsorption process, the adsorbent surface was progressively blocked by dye molecules, becoming covered after some time. The hindrance enhanced with increasing SMT concentration, and thus the time for adsorption equilibrium increased accordingly (41).

When Mahvi et al (42), investigated the adsorption of tetracycline antibiotics onto Azolla, the similar results were also observed. The time attaining equilibrium increased with increasing concentrations. Their study found that 75 min was sufficient to achieve complete recovery of the Penicillin G at initial concentrations below 100 mg/L. However, for the highest concentration (200 mg/L), 90 min was necessary to reach equilibrium. In this work, in order to achieve adsorption equilibrium, the data were measured in 90 min for adsorption isotherms.

4. CONCLUSION: In this paper, investigation of the equilibrium sorption was carried out at 10-55 °C and pH between 6.5 to 7. Other physico-chemical parameters were determined and three adsorption isotherm models were studied. The sorption data fitted into Langmuir, Freundlich and Dubunin–Radushkevich isotherms out of which Langmuir Adsorption model was found to be have the highest regression value and hence the best fit. It could be concluded that rice husk modified with thermally process is a potential and active biosorbent for removal of SMT from its aqueous solution and industrial waste water remediation.

italicize :[6A]Comment

no results for pH effect was :[7A]Comment presented in the paper

REFERENCES

1. Balarak D, Azarpira H, Mostafapour FK. Study of the Adsorption Mechanisms of Cephalexin on to *Azolla Filiculoides*. *Der Pharma Chemica*. 2016;8(10):114-121
2. Peng X, Hu F, Dai H, Xiong Q. Study of the adsorption mechanism of ciprofloxacin antibiotics onto graphitic ordered mesoporous carbons. *J TAIWAN INST CHEM E*. 2016;8:1–10.
3. Balarak D, Kord Mostafapour F. Adsorption of acid red 66 dye from aqueous solution by heat-treated rice husk. *RES J CHEM ENVIRON*. 2018;22(12):80-84.
4. Amini M, Khanavi M, Shafiee A. Simple High-Performance Liquid Chromatographic Method for Determination of Ciprofloxacin in Human Plasma. *Iran J Pharm Res*. 2004;2:99-101.
5. Carabineiro A, Thavorn-Amornsri T, Pereira F, Figueiredo L. Adsorption of ciprofloxacin on surface modified carbon materials. *Water Res*. 2011;45:4583-91.
6. Ibezim EC, Ofoefule SI, Ejeahalaka N, Orisakwe E. In vitro adsorption of ciprofloxacin on activated charcoal and Talc. *Am J Ther*. 1999;6(4):199-201.
7. Ghauch A, Tuğan A, Assi HA: Elimination of amoxicillin and ampicillin by micro scale and nano scale iron particles. *Environ Pollut*. 2009;157:1626–1635.
8. Balarak D, Azarpira H, Mostafapour FK. Adsorption isotherm studies of tetracycline antibiotics from aqueous solutions by maize stalks as a cheap biosorbent. *Int J Pharm Technol*. 2016;8(3):16664-75.
9. Chen WR, Huang CH. Adsorption and transformation of tetracycline antibiotics with aluminum oxide. *Chemosphere*. 2010;79:779–785.
10. Ahmadi S, Banach A, Kord Mostafapour F. Study survey of cupric oxide nanoparticles in removal efficiency of ciprofloxacin antibiotic from aqueous solution: Adsorption isotherm study. *DESALIN WATER TREAT*. 2017;89:297-303.
11. Balarak D, Mostafapour FK. Photocatalytic degradation of amoxicillin using UV/Synthesized NiO from pharmaceutical wastewater. *Indones j chem*. 2019;19(1):211-218.
12. Alexy R, Kumpel T, Kummerer K. Assessment of degradation of 18 antibiotics in the closed bottle test. *Chemosphere*. 2004 ;57:505–512.
13. Balarak, D., Mostafapour, F., Bazrafshan, E., Saleh, T.A. Studies on the adsorption of amoxicillin on multi-wall carbon nanotubes. *WATER SCI TECHNOL*. 2017;75(7):1599-1606
14. Danaloğlu ST, Bayazit ŞS, Kerkez Kuyumcu Ö, Salam MA. Efficient removal of antibiotics by a novel magnetic adsorbent: magnetic activated carbon/chitosan (MACC) nanocomposite. *J Mol Liq*. 2017;240:589–596.
15. Aksu Z, Tunc O. Application of biosorption for Penicillin G removal: Comparison with activated carbon. *Process Biochem*. 2005;40(2):831-47.
16. Ji L, Chen W, Duan L and Zhu D. Mechanisms for strong adsorption of tetracycline to carbon nanotubes: A comparative study using activated carbon and graphite as adsorbents. *Environ Sci Technol*. 2009;43(7):2322–27.

17. Choi KJ, Kim SG, Kim SH. Removal of antibiotics by coagulation and granular activated carbon filtration. *J Hazard Mater.* 2008;151:38–43.
18. Zhang W, He G, Gao P, Chen G: Development and characterization of composite nanofiltration membranes and their application in concentration of antibiotics. *Sep Purif Technol.* 2003;30:27–35.
19. Balarak D, Azarpira H. Rice husk as a Biosorbent for Antibiotic Metronidazole Removal: Isotherm Studies and Model validation. *International Journal of Chem Tech Research.* 2016;9(7):566-573.
20. Yu F, Li Y, Han S, Jie Ma J. Adsorptive removal of antibiotics from aqueous solution using carbon Materials. *Chemosphere.* 2016;153:365–385.
21. Zhang L, Song X, Liu X, Yang L, Pan F. Studies on the removal of tetracycline by multi-walled carbon nanotubes, *Chem Eng J.* 2011;178:26–33.
22. Yalçın N, Sevinç V. Studies of the surface area and porosity of activated carbons prepared from rice husks. *Carbon.* 2000;38(14):1943–1945.
23. Guo Y, Yu K, Wang, Z, Hongding Xu H. Effects of activation conditions on preparation of porous carbon from rice husk. *Carbon.* 2003;41(8):1645–1648
24. Li M, Shu D, Jiang L. Cu (II)-influenced adsorption of ciprofloxacin from aqueous solutions by magnetic graphene oxide/nitrilotriacetic acid nanocomposite: competition and enhancement mechanisms. *Chem Eng J.* 2017; 319:219–228.
25. Liu H, Liu W, Zhang J, Zhang C, Ren L, Li Y. Removal of cephalexin from aqueous solution by original and Cu(II)/Fe(III) impregnated activated carbons developed from lotus stalks kinetics and equilibrium studies. *J Hazard Mater.* 2011;185:1528–35.
26. Putra EK, Pranowoa R, Sunarsob J, Indraswatia N, Ismadjia S. Performance of activated carbon and bentonite for adsorption of amoxicillin from wastewater: mechanisms, isotherms and kinetics. *Water Res.* 2009;43:2419-2430.
27. Balarak D, Azarpira H. Biosorption of Acid Orang 7 using dried *Cyperus Rotundus*: Isotherm Studies and Error Functions. *International Journal of Chem Tech Research.* 2016; 9(9):543-9.
28. Liu Z, Xie H, Zhang J, Zhang C. Sorption removal of cephalexin by HNO₃ and H₂O₂ oxidized activated carbons. *Sci China Chem.* 2012;55:1959–67.
29. Liu W, Zhang J, Zhang C, Ren L. Sorption of norfloxacin by lotus stalk-based activated carbon and iron-doped activated alumina: mechanisms, isotherms and kinetics. *Chem Eng J.* 2011;171(2):431–438.
30. Hu D and L. Wang, Adsorption of amoxicillin onto quaternized cellulose from flax noil: Kinetic, equilibrium and thermodynamic study. *J Taiwan Inst. Chem Eng.* 2016;64:227-234.
31. Wang F, Yang B, Wang H, Song Q, Tan F, Cao Y. Removal of ciprofloxacin from aqueous solution by a magnetic chitosan grafted graphene oxide composite. *J Mol Liq.* 2016;222:188–194.
32. Shokohi R, Jafari SJ, Saidi S, Ghamar N, Siboni M. Removal dye Acid Blue 113(AB113) dye from aqueous environment by adsorption on Activated Redmud. *Kordestan Univ Med Sci J.* 2011;16(2):55-65.
33. Peterson JW, Petrasky LJ, Seymourc MD, Burkharta RS, Schuilinga AB. Adsorption and breakdown of penicillin antibiotic in the presence of titanium oxide nanoparticles in water. *Chemosphere.* 2012;87(8):911–7.

34. Kyzas GZ, Bikiaris DN, Seredych M, Bandosz TJ, Deliyanni EA. Removal of dorzolamide from biomedical wastewaters with adsorption onto graphite oxide/poly(acrylic acid) grafted chitosan nanocomposite. *Bioresour Technol.* 2014;152:399–406.
35. 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):138-45.
36. Balarak D. Kinetics, Isotherm and Thermodynamics Studies on Bisphenol A Adsorption using Barley husk. *International Journal of Chem Tech Research.* 2016;9(5):681-90.
37. Adrianoa WS, Veredasb V, Santanab CC, Gonçalves LRB. Adsorption of amoxicillin on chitosan beads: Kinetics, equilibrium and validation of finite bath models. *Biochem Eng J.* 2005;27(2):132-37.
38. Gao J and Pedersen JA. Adsorption of Sulfonamide Antimicrobial Agents to Clay Minerals. *Environ Sci Technol.* 2005;39(24):9509-16.
39. Diyanati RA, Yousefi Z, Cherati JY, Balarak D. Investigating phenol absorption from aqueous solution by dried azolla. *J MAZANDRAN UNIV MED SCI.* 2013;22(2):13-21.
40. Diyanati RA, Yousefi Z, Cherati JY, Balarak D. The ability of Azolla and lemna minor biomass for adsorption of phenol from aqueous solutions. *J MAZANDRAN UNIV MED SCI.* 2013;23(106):17-23.
41. Azarpira H, Mahdavi Y, Khaleghi O. Thermodynamic Studies on the Removal of Metronidazole Antibiotic by Multi-Walled Carbon Nanotubes. *Der Pharm. Lett.* 2016;8(11):107-13.
42. Mahvi AH, Mostafapour FK, Balarak D. Biosorption of tetracycline from aqueous solution by azolla filiculoides: equilibrium kinetic and thermodynamics studies. *Fresenius Environ. Bull.* 2018;27(8):5759-5767.