



Langmuir, Freundlich, Temkin and Dubinin–radushkevich Isotherms Studies of Equilibrium Sorption of Ampicilin unto Montmorillonite Nanoparticles

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Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

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ABSTRACT

Present study was accomplished to prospect the viability of using the montmorillonite (Mon) nanoparticles as an adsorbent to remove the Ampicillin under various experimental conditions. The Physico-chemical characteristics of the studied adsorbent were surveyed. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms were applied to portray the data obtained from the adsorption studies. The findings showed that the highest R^2 values were related to Langmuir and Dubinin–Radushkevich isotherm models. The greatest adsorption capacity (q_e) for Langmuir and Dubinin–Radushkevich isotherm models were recognized to be 134.48 mg/g and 141.22 mg/g, respectively; and the separation factor was calculated to be 0.113 which is indicative of a favorable

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sorption. Temkin Isotherm model clarified that the heat of sorption process was 34.61 J/mol; and the mean free energy calculated by Dubinin–Radushkevich isotherm model was anticipated to be 2.56 KJ/mol which these undoubtedly demonstrate the physisorption process for Ampicillin adsorption experiments.

Keywords: Montmorillonite nanoparticles; ampicillin; isotherm.

1. INTRODUCTION

Antibiotics are the most extensively used drugs to prevent or treat bacterial infections in humans, animals and plants [1,2]. Antibiotics discharged from wastewater treatment plants (WWTPs) and as through effluents from pharmaceutical manufacturing plants to the environment have received a growing concern because of their potential toxic effect on the aquatic biota as well as human [3,4]. Ampicillin is a common antibiotic used in human and animal medicine, and is an amphoteric, beta-lactam of the penicillin class [5]. The Ampicillin is one of the most commonly used antibiotics at Iran and worldwide, which finds wide applications in human therapy and the livestock industry, and is difficult to be metabolized [6-8].

The presence of antibiotics in the environment has, therefore, received considerable attention [9]. It has been found that antibiotics are, in general, poorly absorbed by the human body and, thus, are excreted either unchanged or as their metabolites via urine and feces [10,11]. Furthermore, most antibiotics are highly toxic, soluble in water and of low biodegradability [12].

Removing antibiotics is difficult and requires expensive process. In recent years, there has been an increasing interest to the treatment of pollution generated by drug residues, including antibiotics [13,14]. Physical and Physico-chemical and biological techniques have proved their efficiency for this purpose [15,16]. The Physical and Physico-chemical techniques used for antibiotics removal from wastewater include ozonation, flocculation, electro-flocculation, reverse osmosis, ultrafiltration, coagulation and photodegradation process [17,18]. These most conventional methods are non-destructive and merely transfer pollutants from one phase to the other, which always result in secondary pollution [19,20]. Also Biological processes, the most cost-effective for wastewater treatment, which are destructive and have been extensively studied do not always, appear relevant for the removal of recalcitrant compounds, owing to their low biodegradability [21].

Of these methods, sorption has proved to be an attractive process because of its low cost and ease of operation [22,23]. Activated carbon has been widely used for this purpose because of its high adsorption capacity [24]. However, its high cost sometimes tends to limit its use. Clays are widely applied in many fields such as polymer nano-composites, adsorbents for pollutant ions, catalysts, photochemical reaction fields, sensors and biosensors, due to their high specific surface area, chemical and mechanical stabilities, and a variety of surface and structural properties [25-27].

Clay is a potentially good adsorptive material because of its large surface area, chemical and mechanical stability, and layered structure [27]. The adsorption of pollutant into natural clays has recently been studied by various researchers. Among natural clays, montmorillonite acts as a adsorbent for pollutant due to its low-cost, high abundance, easy manipulation, and harmlessness to the environment [28]. The most-used clays as nano-adsorbents are montmorillonite group and kaolinite group clays [29]. In this paper, the possibility of using montmorillonite nanoparticles to remove Ampicillin was investigated using batch adsorption studies. The equilibrium data were analyzed so that we can understand the adsorption mechanism and different models (Langmuir, Freundlich, and Temkin and Dubinin–Radushkevich) were applied to fit the experimental data.

2. MATERIALS AND METHODS

Ampicillin (CAS Number 69-53-4; chemical formula, $C_{16}H_{19}N_3O_4S$; MW, 349.40 g/mol) was used as the adsorbate in this study obtained from Sigma Aldrich Co; it was used without further purification. The chemical structure of Ampicillin, shown in Fig. 1.

Ampicillin stock solution was prepared by dissolving an accurately weighed amount of Ampicillin in distilled water to achieve a concentration of 200 mg/L, and subsequently diluted to the required concentrations. All

chemicals used in this study were of analytical-laboratory grade, being purchased from Merck.

A montmorillonite nanoparticle was obtained from the Iranian nanosany Corporation and was used without further purification. Chemical analysis of the clay was carried out using an X-ray fluorescence spectrometer (XRF-Philips PW2400). BET surface area and total pore volume of the clay were measured using Autosorb-1 (Quantachrome Corporation, New York), with N₂ gas as the adsorbate.

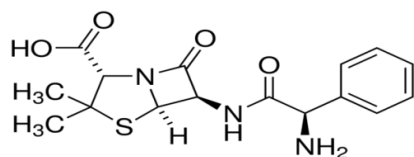


Fig. 1. The chemical structure of Ampicillin

2.1 Adsorption Experiments

Adsorption experiments were carried out by batch method at room temperature. The time-dependent behavior of Ampicillin adsorption was studied by varying the contact time between the adsorbate and adsorbent in the range 10-120 min. The initial concentration of Ampicillin was kept at 25 mg/L, while the dose of Mon-nanoparticles was 0.5 g/L. At the end of each adsorption experiment, the solution and solid phase were separated by centrifugation at 4000

rpm for 15 min. Ampicillin concentration at samples was determined by a High Performance Liquid Chromatography (HPLC) (Agilent 1100 Series) at wavelength 204 nm. The mobile phase was 60% 0.025 M KH₂PO₄ buffer solution in ultra pure water and 40% acetonitrile at a flow rate of 0.50 mL/min.

The adsorption capacity of Ampicillin on adsorbent was calculated using the following equation [30,31]:

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

Where C₀ and C_e are the Ampicillin concentrations in mg/L initially and at a given time t, respectively, V is the volume of Ampicillin solution in L, and M is the weight of sorbent in g.

3. RESULTS AND DISCUSSION

The Tables 1 and 2 represented the chemical composition and physicochemical properties of the Mon-nanoparticles, respectively. As it can be seen in Table 1, Montmorillonite has considerable levels of SiO₂ (57.7%) and Al₂O₃ (18.1%) and the quantity of other metal oxides is observed to be lesser than 20%. The investigation of the surface physical morphology of Montmorillonite was fulfilled using the scanning electron microscopy (SEM) technique. Fig. 2 shows the SEM images of the Montmorillonite. Furthermore, it was found that the surface area of Montmorillonite is 245.5 m²/g.

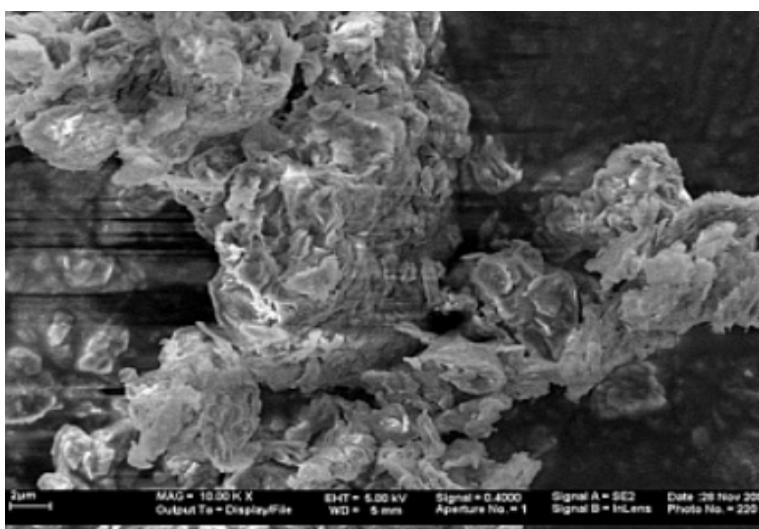


Fig. 2. SEM micrographs of the Montmorillonite samples

Table 1. Chemical compositions of Mon-nanoparticles

Component	%
SiO ₂	57.7
Al ₂ O ₃	18.1
Fe ₂ O ₃	7.25
MgO	3.11
CaO	1.64
Na ₂ O	1.22
TiO ₂	0.68
MnO	0.29
LOI	9.25

Table 2. Physicochemical properties of Mon-nanoparticles

Parameter	Value
BET surface area	245.5 m ² /g
Total pore volume	2.14×10 ⁻³ cm ³ /g
Average pore diameter	51 (Å)
Particle size	1-2 nm
Moisture	1-2%

3.1 Adsorption Isotherms

The adsorption data were analyzed to see whether the isotherm obeyed the Langmuir, Freundlich, Dubinin-Radushkevich (D-R) and Temkin isotherm models equations [32-36]:

$$\text{Langmuir equation} = \frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} K_L} \times \frac{1}{C_e}$$

$$\text{Freundlich equation} = \text{Log } q_e = \frac{1}{n} \text{log } C_e + \text{log } K_F$$

$$\text{D-R equation: } \text{Ln } q_e = \text{Ln } q_m - \beta \epsilon^2$$

$$\text{Temkin equation: } q_e = \frac{RT}{b} \text{Ln } A + \frac{RT}{b} \text{Ln } C_e \quad B = \frac{RT}{b}$$

Where q_{\max} , the monolayer capacity of the adsorbent (mg/g); K_L , the Langmuir constant (L/mg) and related to the free energy of adsorption; q_m , the theoretical saturation capacity (mg/g); and ϵ , the Polanyi potential, which is equal to $RT \text{Ln} (1 + (1/C_e))$, where R (J/mol K) is the gas constant and T (K) is the absolute temperature; β , a constant related to the mean free energy of adsorption per mole of the adsorbate (mol²/kJ²). For Freundlich isotherm, K_F is the adsorption capacity at the unit concentration (L/g) and $\frac{1}{n}$ is adsorption intensity.

$\frac{1}{n}$ Values specify whether isotherm is irreversible ($\frac{1}{n} = 0$), favorable ($0 < \frac{1}{n} < 1$) or unfavorable

($\frac{1}{n} > 1$). For Temkin isotherm, the A , b , R , T are equilibrium binding constant (L/g) Temkin isotherm constant, universal gas constant (8.314 J/mol K) and temperature at 298 K, respectively. B is constant related to the heat of sorption (J/mol).

The linear plot of $1/C_e$ versus $1/q_e$ (Fig. 3a) is utilized to calculate the q_{\max} and K_L in Langmuir equation. The calculation of q_m and β of D-R equation is performed by plotting $\text{Ln } q_e$ versus ϵ^2 (Fig. 3b). K_F and $1/n$ of Freundlich equation are achieved from the slope and intercepts of the linear plot of $\text{log } q_e$ versus $\text{log } C_e$ (Fig. 3C).

Temkin isotherm contains a factor that is explicitly entered into the adsorbent-adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage. As implied in the equation, its derivation is characterized by a uniform distribution of binding energies (up to some maximum binding energy) was carried out by plotting the quantity sorbed q_e against $\text{Ln } C_e$ and the constants were determined from the slope and intercept (Fig. 3d).

The Langmuir, Freundlich, Temkin and D-R parameters for the adsorption of Ampicillin onto Mon-nanoparticles were listed in Table 3. The comparison of R^2 represented in Table 3 advocates that D-R and Langmuir model have more facility to portray the data compared to Temkin and Freundlich models.

The constant β is related to the mean free energy E (kJ/mol) of adsorption per molecule of the adsorbate when it is moved to the surface of the solid from the solution. It is calculated by the following relationship [37-40]:

$$E = \frac{1}{(2\beta)^{1/2}}$$

Where β is represented as the isotherm constant. Based on the linear plot obtained from D-R model, the q_m was determined to be 141.22 mg/g; the mean free energy, E , was observed to 2.56 KJ/mol which this value indicates the adsorption of Ampicillin is a physisorption process. The R^2 value for this isotherm model was calculated to be 0.991.

Also considering the Table 3, the values of $1/n = 0.425$ and $n=2.35$ indicate the favorable sorption

of Ampicillin unto Mon-nanoparticles; the R^2 value is achieved to be 0.82.

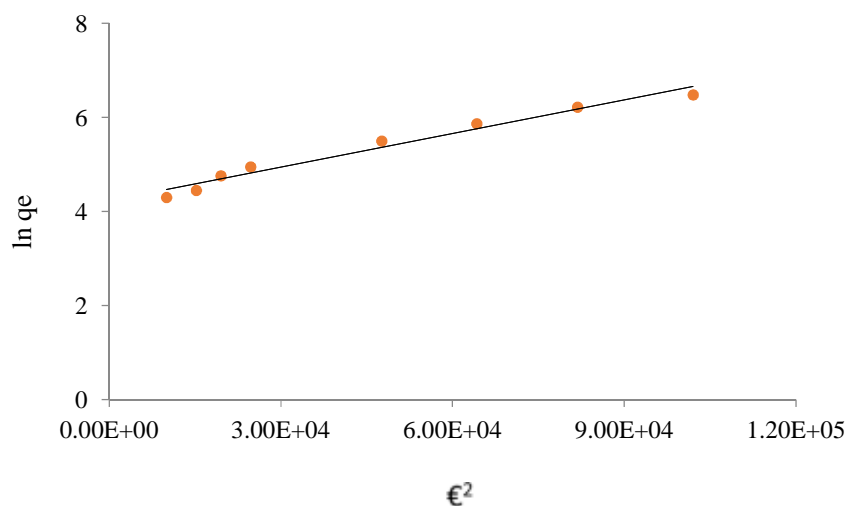
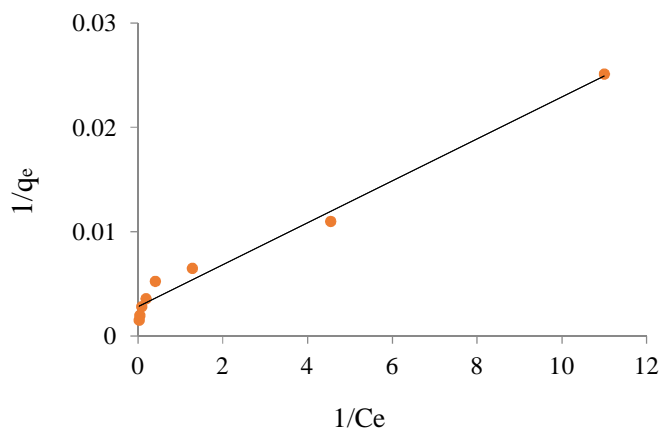
Moreover, Table 3 shows that the values of A and B is 1.85 L/g and 34.61 J/mol, respectively which is indicative of the adsorption heat and a physical adsorption process; the R^2 was found to be 0.84.

The critical properties of the Langmuir isotherm may be affirmed from viewpoint of equilibrium parameter R_L , which is a dimensionless constant related to separation factor or equilibrium parameter [41-44]:

$$R_L = \frac{1}{1 + (1 + K_L C_e)}$$

K_L is considered as the constant referred to the adsorption energy (Langmuir Constant). R_L is a

value that reveals the adsorption nature so that the adsorption could be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) and irreversible ($R_L = 0$). According to the data represented in Table 3, the favorable Langmuir isotherm is observed for R_L values greater than 0 and lesser than 1. Furthermore, the maximum monolayer coverage capacity (q_{max}), which is calculated by the Langmuir Isotherm model, was obtained to be 134.48 mg/g and K_L (Langmuir isotherm constant) is 0.047 L/mg. R_L (the separation factor) is 0.254 and it shows that the equilibrium sorption was favorable; and the R^2 value is 0.989 and it is confirmed that the sorption data was appropriately fitted to Langmuir Isotherm model. Table 4 depicts the maximum adsorption capacities (q_{max}) of some adsorbents for the better understanding of the adsorbent performance.



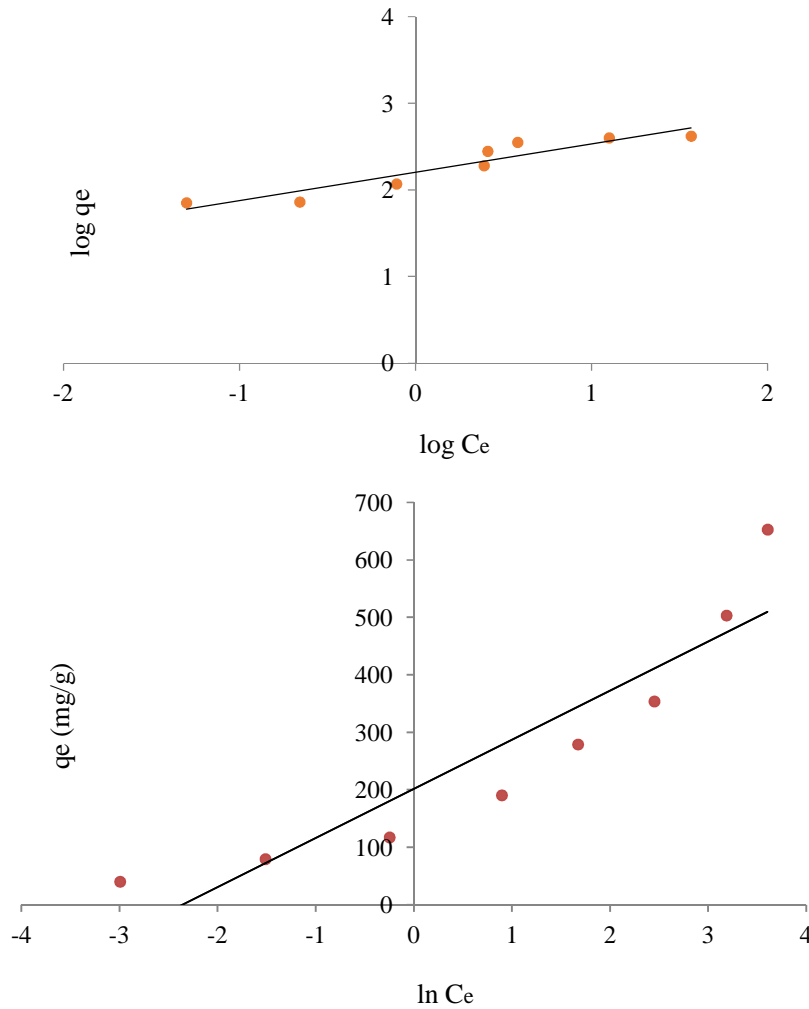


Fig. 3. a: Langmuir, b: D-R C: Freundlich and d: Temkin adsorption isotherms of Ampicillin Mon-nanoparticles

Table 3. Isotherms constants for the removal AMX onto Pumice

Langmuir model				Freundlich model		
q_m (mg/g)	R_L	K_L	R^2	n	K_F	R^2
134.48	0.254	0.0047	0.989	2.35	4.571	0.821
D-R model				Temkin model		
q_m (mg/g)	β	E	R^2	B	A	R^2
141.22	0.0062	2.56	0.991	34.61	1.85	0.842

Table 4. Maximum adsorption capacities (q_{max}) of some adsorbents for different antibiotics

Adsorbent	Antibiotic	q_{max} (mg/g)	Ref
Mon-nanoparticles	Ampicillin	134.48	present work
Azolla filiculoides	Sulfamethoxazole	17.25	[1]
Activated Carbon	Ciprofloxacin	242.8	[2]
Clay	Sulfonamide	46.29	[3]
MWCNS	Tetracycline	196.4	[10]

Adsorbent	Antibiotic	q _{max} (mg/g)	Ref
MWCNS	Metronidazole	266.7	[11]
MWCNS	Amoxicillin	159.4	[12]
Lemna minor	Penicillin G	26.17	[18]
Alumina-coated-MWCNT	Tetracycline	347.9	[20]
MgO nanoparticles	Cephalexin	500	[45]
Organobentonite	Amoxicillin	30.12	[46]

4. CONCLUSION

The present study shows that the Mon-nanoparticles were successfully used as an adsorbent for the quantitative removal of Ampicillin from aqueous solutions. The experimental adsorption equilibrium data of Ampicillin on Mon-nanoparticles were compared with the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich models and adsorption capacities were determined. These results showed that Langmuir and D–R isotherm model was better than Freundlich and Temkin model.

CONSENT

It is not applicable.

ETHICAL APPROVAL

It is not applicable.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

- Balarak D, Mostafapour FK. Batch equilibrium, kinetics and thermodynamics study of sulfamethoxazole antibiotics onto *Azolla filiculoides* as a novel biosorbent. *British Journal of Pharmaceutical Research*. 2016;13(2):1-14.
- Balarak D, Mostafapour FK, Azarpira H. Adsorption kinetics and equilibrium of ciprofloxacin from aqueous solutions using *Corylus avellana* (Hazelnut) activated carbon. *British Journal of Pharmaceutical Research*. 2016;13(3):1-14.
- Gao J, Pedersen JA. Adsorption of sulfonamide antimicrobial agents to clay minerals. *Environ. Sci. Technol*. 2005;39(24):9509-16.
- Peterson JW, Petrasky LJ, Seymour MD, Burkhardt RS, Schuilinga AB. Adsorption and breakdown of penicillin antibiotic in the presence of titanium oxide nanoparticles in water. *Chemosphere*. 2012;87(8):911–7.
- Balarak D, Mostafapour FK, Akbari H, Joghtaei A. Adsorption of amoxicillin antibiotic from pharmaceutical wastewater by activated carbon prepared from *Azolla filiculoides*. *British Journal of Pharmaceutical Research*. 2017;18(3):1-11.
- Balarak D, Joghataei A, Azarpira H, Mostafapour FK. Biosorption of amoxicillin from contaminated water onto palm bark biomass. *International Journal of Life Science and Pharma Research*. 2017;7(1): 9-16.
- 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.
- 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.
- Yu F, Li Y, Han S, Jie Ma J. Adsorptive removal of antibiotics from aqueous solution using carbon materials. *Chemosphere*. 2016;153:365–385.
- 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.
- Azarpira H, Mahdavi Y, Khaleghi O, Balarak D. Thermodynamic studies on the removal of metronidazole antibiotic by multi-walled carbon nanotubes. *Der Pharmacia Lettre*. 2016;8(11):107-13.
- Balarak D, Mostafapour FK, Bazrafshan E, Saleh TA. Studies on the adsorption of amoxicillin on multi-wall carbon nanotubes. *Water Science and Technology*. 2017;75(7):14-20.
- Choi KJ, Kim SG, Kim SH. Removal of antibiotics by coagulation and granular activated carbon filtration. *J. Hazard. Mater*. 2008;151:38–43.
- 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.
15. 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.
 16. Ghauch A, Tuqan A, Abou AH. Antibiotic removal from water: Elimination of amoxicillin and ampicillin by microscale and nanoscale iron particles. *Environ. Pollut.* 2009;157:1626–1635.
 17. 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.
 18. Balarak D, Mostafapour FK, Joghataei A. Experimental and kinetic studies on penicillin G adsorption by *Lemna minor*. *British Journal of Pharmaceutical Research.* 2016;9(5):1-10.
 19. Balarak D, Mahdavi Y, Maleki A, Daraei H, Sadeghi S. Studies on the removal of amoxicillin by single walled carbon nanotubes. *British Journal of Pharmaceutical Research.* 2016;10(4):1-9.
 20. Balarak D, Mahdavi Y, 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.
 21. Alexy R, Kumpel T, Kummerer K. Assessment of degradation of 18 antibiotics in the closed bottle test. *Chemosphere.* 2004;57:505–512.
 22. Carabineiro A, Thavorn-Amornsri T, Pereira F, Figueiredo L. Adsorption of ciprofloxacin on surface modified carbon materials. *Water Res.* 2011;45:4583-91.
 23. 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.
 24. Peng X, Hu F, Dai H, Xiong Q. Study of the adsorption mechanism of ciprofloxacin antibiotics onto graphitic ordered mesoporous carbons. *Journal of the Taiwan Institute of Chemical Engineers.* 2016;8:1–10.
 25. Almeida CAPJ, Debacher NA, Downs AJ, Cottet L, Mello CAD. Removal of methylene blue from colored effluents by adsorption on montmorillonite clay. *Journal of Colloid and Interface Science.* 2009;332:46–53.
 26. Yue QY, Li Q, Gao BY, Yuan AJ, Wang Y. Formation and characteristics cationic-polymer/ bentonite complexes of as adsorbents for dyes. *Appl. Clay Sci.* 2007;35:268–275.
 27. Rytwo G, Huterer-Harari R, Dultz S, Gonen Y. Adsorption of fast green and erythrosin-B to montmorillonite modified with crystal violet. *J Therm Anal. Calor.* 2006;84:225–231.
 28. Yermiyahu Z, Lapides I, Yariv S. Visible absorption spectroscopy study of the adsorption of Congo Red by montmorillonite. *Clay Miner.* 2003;38:483–500.
 29. Teng MY, Lin SH. Removal of basic dye from water onto pristine and HCl-activated montmorillonite in fixed beds. *Desalination.* 2006;194:156–165.
 30. Balarak D, Mostafapour FK, Joghtaei A. Thermodynamic analysis for adsorption of amoxicillin onto magnetic carbon nanotubes. *British Journal of Pharmaceutical Research.* 2017;16(6):1-11.
 31. Ghauch A, Tuqan A, Assi HA. Elimination of amoxicillin and ampicillin by micro scale and nano scale iron particles. *Environ Pollut.* 2009;157:1626–1635.
 32. Senthilkumaar S, Varadarajan PR, Porkodi K, Subbhuraam CV. Adsorption of methylene blue onto jute fiber carbon: Kinetics and equilibrium studies. *J. Colloid Interface Sci.* 2005;284:78–82.
 33. Aksu Z, Tunc O. Application of biosorption for penicillin G removal: Comparison with activated carbon. *Process Biochemistry.* 2005;40(2):831-47.
 34. Ji L, Chen W, Duan L, 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.
 35. Zazouli MA, Mahvi AH, Mahdavi Y, Balarak D. Isothermic and kinetic modeling of fluoride removal from water by means of the natural biosorbents sorghum and canola. *Fluoride.* 2015;48(1):15-22.
 36. Balarak D, Mostafapour FK. Biosorption of acid green 25 from textile dye effluent using barley husk. *International Journal of*

- Advanced Biotechnology and Research. 2017;8(1):128-135.
37. 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*. 2015;7:16–19.
 38. 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):35-42.
 39. Zazouli MA, Mahvi AH, Dobaradaran S, Barafrahshtehpour M, Mahdavi Y, Balarak D. Adsorption of fluoride from aqueous solution by modified *Azolla filiculoides*. *Fluoride*. 2014;47(4):349-58.
 40. 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 filiculoides*. *Fresenius Environmental Bulletin*. 2016;25(5):1321-30.
 41. Uddin MT, Islam MA, Mahmud S, Rukanuzzaman M. Adsorptive removal of methylene blue by tea waste. *J. Hazard. Mater*. 2009;164:53–60.
 42. Agarwal S, Tyagi I, Gupta VK, Dehghani MH, Jaafari J, Balarak D. Rapid removal of noxious nickel (II) using novel gamma-alumina nanoparticles and multiwalled carbon nanotubes: Kinetic and isotherm studies. *Journal of Molecular Liquids*. 2016;224:618-623.
 43. Balarak D, Mostafapour FK, Azarpira H. Biosorption of reactive blue 19 dye using *Lemna minor*: Equilibrium, kinetic and thermodynamic studies. *Bioscience Biotechnology Research Communications*. 2016;9(3):558-566.
 44. Balarak D, Bazrafshan E, Mahdavi Y, Lee SM. Kinetic, isotherms and thermodynamic studies in the removal of 2-chlorophenol from aqueous solution using modified rice straw. *Desalination and Water Treatment*. 2017;63:203-211.
 45. Fakhri A, Adami S. Adsorption and thermodynamic study of cephalosporins antibiotics from aqueous solution onto MgO nanoparticles. *Journal of the Taiwan Institute of Chemical Engineers*. 2014; 45(3):1001–1006.
 46. Zhou SX, Jin Y, Chen X. The removal of amoxicillin from wastewater using organobentonite. *Journal of Environmental Management*. 2013;129:569–576.

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