Journal of Materials and Environmental Science
ISSN : 2028-2508
CODEN : JMESCN

J. Mater. Environ. Sci., 2020, Volume 11, Issue 11, Page 1839-1845

http://www.jmaterenvironsci.com

Adsorption of aspirin onto biomaterials from aqueous solutions

Abdoulaye Demba N'diaye [1,2*] and **Mohamed Sid'Ahmed Kankou** [1]

[1] *Unité de Recherche Eau, Pollution et Environnement, Département de Chimie, Faculté des Sciences et Technique, Université de Nouakchott Al Aasriya, BP 880, Nouakchott, Mauritanie*

[2] *Laboratoire de Chimie, Service de Toxicologie et de Contrôle de Qualité, Institut National de Recherches en Santé Publique, BP 695, Nouakchott, Mauritanie*

Received 04 June 2020,
Revised 23 July 2020,
Accepted 02 Aug 2020

Keywords:
- *Aspirin,*
- *Zizyphus Mauritiana* seeds
- *Balanites Aegyptiaca* seeds
- Biomaterials,
- Isotherms

abdouldemba@yahoo.fr;
Phone: +222 4163 92 52

Abstract

The aim of this study is to investigate the adsorption of aspirin from aqueous solutions using *Zizyphus Mauritiana* seeds and *Balanites Aegyptiaca* seeds as low cost adsorbents. The equilibrium data were analyzed using nonlinear method by fitting them to the Langmuir, Freundlich and Jovanovic model equations. The Sum of the Squares of the Errors (SSE) and the correlation coefficients (R^2) between the calculated data and the experimental data by nonlinear method were used. The best fitting isotherm was found to be the Langmuirr isotherm. Maximum adsorption capacities were found to be 8.95 and 7.40 mg g^{-1} at *Zizyphus Mauritiana* seeds and *Balanites Aegyptiaca* seeds, respectively. The present study showed that the *Zizyphus Mauritiania* seeds and *Balanites Aegyptiaca* seeds without any treatment can be considered promising biomaterials to be used for pharmaceutical products adsorption.

1. Introduction

Pharmaceutical products are widely consumed by humans to prevent or treat diseases. However, many studies reported that pharmaceutical products and its metabolites are commonly detected in wastewater, sewage, surface water, ground water and even drinking water [1-5].

The impact on the environment and public health arises not only from wastewater effluents discharged in aquatic media [6], but also from sludge application in agriculture [7]. Among the pharmaceutical products, the aspirin is one of the most consumed and produced pharmaceutical product [8].

Several methods such as advanced oxidation processes [9], biodegradation [10], membrane filtration [11] and adsorption [12] have shown positive results in removing the pharmaceutical products. Adsorption is found as the most promising removal method because of its versatility in removing different pollutant and also its efficiency [13].

However, due to the cost of commercial activated carbon, many researchers have concentrated on finding alternative natural adsorbents to activated carbon such as Sugar Can Bagasse [14], Vegetable Sponge [14], grape stalk [15], yohimbe bark [15], cork bark [15], *Posidonia Oceanica* [16], Dehydrated sewage sludge [16], Banana peel [17], Grape Stalk [18], *Zizyphus Mauritiana* seeds [19], *Balaanites aegyptiaca* seeds [20] and groundnut shell [21] for removing pharmaceutical products present in aqueous medium.

The aim of our study were to investigate the potential of using *Zizyphus Mauritiana* seeds and *Balanites Aegyptiaca* seeds, as a low cost adsorbents to remove aspirin from aqueous solutions, to model the equilibrium of the process. The retention capacity of aspirin onto the *Zizyphus Mauritiana* seeds and

Balanites Aegyptiaca seeds is investigated with using the nonlinear two-parameter models (Langmuir, Freundlich and Jovanovic). So, the adsorption parameters obtained using the present adsorbents will be compared with the ones presented in the literature.

2. Material and Methods

2.1 Asborbate, adsosbents and experimental procedures

All the solutions are prepared using aspirin and distilled water. The stock solution is prepared by adding 500 mg of the active ingredient to 500 mL of distilled water. Other concentrations are prepared by dilutions of the stock solution and used to develop the standard curves [12].

Zizyphus Mauritiana seeds and *Balanites Aegyptiaca* seeds were collected from the south of Mauritania. Details on the preparation of the adsorbents from residues, as well as some characterization parameters of the *Zizyphus Mauritiana* seeds (Figure 1.a) and *Balanites Aegyptiaca* seeds (Figure 1.b) have been reported in previous studies [19; 20].

a)  **b)** 

Figure 1: a) *Zizyphus Mauritania* seeds b) *Balanites Aegyptiaca* seeds

Some physico- chemical characteristics of the *Zizyphus Mauritiana* seeds and *Balanites aegyptiaca* seeds are given in Table 1 [19; 20].

Table 1. Physicochemical characteristics of the studied biomaterials

Parameters	***Zizyphus Mauritiana* seeds**	***Balanites Aegyptiaca* seeds**
pH_{pzc}	6.9	5.8
Moisture (%)	4.2	3.9
Ash (%)	7.5	5.7
Volatile matter (%)	76.20	78.20
Cellulose (%)	11.5	41.3
Hemicellulose (%)	4.6	33.9
Lignin (%)	7.5	15.2
Particle size (µm)	<100	<100

2.2 Adsorption isotherms

The adsorption isotherms at ambient temperature are obtained by mixing (70 rpm), for 180 minutes, 0.5 g of adsorbent with 50 mL of aspirin solutions with different concentrations varying from 0 to 100 mg L^{-1}. At the end of each experiment the agitated solution mixture was micofiltered using micro filter and the residual concentration of aspirin was determined by High Performance Liquid Chromatography (HPLC). Mixture of acetonitrile-water (25:75 v/v) adjusted to pH 2.5 with phosphoric acid was used as a mobile phase at a flow rate of 2 mL min^{-1}at a selected wave length of 222 nm [12]. The adsorbed quantity at equilibrium (q_e) is calculated according to the following equation (1):

$$q_e = \frac{(C_i - C_e)V}{m} \qquad (1)$$

Where
- q_e: quantity of aspirin per g of adsorbent (mg g^{-1}),
- C_i: initial solution concentration of aspirin (mg L^{-1}),
- C_e: equilibrium solution concentration of aspirin (mg L^{-1}),
- m: the adsorbent weight (g),

Adsorption isotherms, which are a common name of equilibrium relationships, are essential for optimization of the adsorption mechanism pathways [22; 23].
Three different models are used (Table 2) and classified into:
-Simple isotherm models for homogeneous surfaces, like Langmuir equation [24] and Jovanovic equation [25];
-Isotherm models for heterogeneous surfaces, like Freundlich equation [26].

Table 2. Mathematical equation of the isotherm models

Model	Equation	Parameter and dimension
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	q_m: maximum solute adsorbed at equilibrium state (mg g^{-1}) and K_L: Langmuir coefficient (mg L^{-1})
Freundlich	$q_e = K_F C_e^{1/n}$	K_F: Freundlich coefficient (mg g^{-1}).(mg L^{-1})$^{-n}$ and n: model exponent (–)
Jovanovic	$q_e = q_m(1 - e^{-K_J C_e})$	q_m: Jovanovic constant related to the adsorption capacity(mg g^{-1}) and K_J: Jovanovic constant related to the rate of adsorption (L mg^{-1}).

The factor of separation of Langmuir, R_L, which is an essential factor characteristic of this isotherm is calculated by using the relation (2):

$$R_L = \frac{1}{(1 + k_L C_0)} \qquad (2)$$

C_0 is the higher initial concentration of aspirin and K_L is the Langmuir constant. The R_L value implies the adsorption to be defavourable (R_L>1), linear (R_L=1), favourable (0<R_L<1), or irreversible (R_L=0).
The Sum of the Squares of the Errors (SSE) and the correlation coefficients (R^2) analysis is used to fit experimental data with isotherm using the Excel Solver. The SSE and R^2 values are determined respectively by following equations (3) and (4):

$$\text{SSE} = (q_{exp} - q_{mod})^2 \qquad (3)$$

$$R^2 = 100\left(1 - \frac{\|q_{exp} - q_{mod}\|^2}{\|q_{exp} - q_{avr}\|^2}\right) \qquad (4)$$

Where q_{exp} (mg g^{-1}) is equilibrium capacity from the experimental data, q_{avr} (mg g^{-1}) is equilibrium average capacity from the experimental data and q_{mod} (mg g^{-1}) is equilibrium from model. So that $R^2 \leq$ 100 – the closer the value is to 100, the more perfect is the fit.

3. Results and discussion

The adsorption isotherm gives an idea of the equilibrium behavior of an adsorbate–adsorbent system. The isotherm curves of aspirin adsorption onto *Zizyphus Mauritiana* seeds and *Balanites Aegyptiaca* seeds are studied and represented in Figures 2 and 3 and then modeled using the isotherm equations of Langmuir, Freundlich and Jovanovic. Isotherm model parameters are given in Table 3.

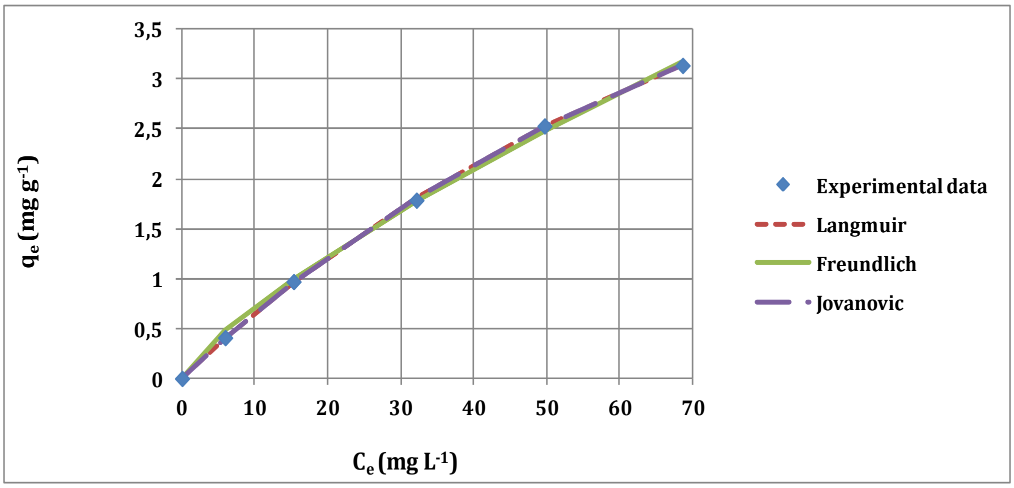

Figure 2: Langmuir, Freundlich and Jovanovic nonlinear for *Zizyphus Mauritiana* seeds

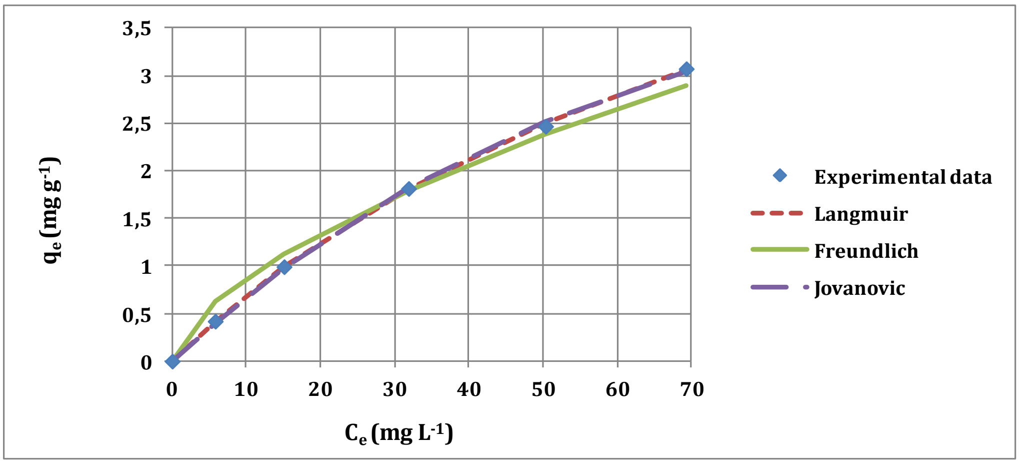

Figure 3: Langmuir, Freundlich and Jovanovic non linear for *Balanites Aegyptiaca* seeds

Table 3. Parameters isotherm model for aspirin retention on the adsorbents

sModel	**Parameters**	***Zizyphus Mauritiana* seeds**	***Balanites Aegyptiaca* seeds**
Langmuir	**q_m**	8.95	7.40
	K_L	0.0079	0.010
	R_L	0.56	0.50
	SSE	0.0008	0.0017
	^{2}R (%)	99.98	99.96
Freundlich	**1/n**	0.77	0.62
	K_F	0.122	0.209
	SSE	0.0104	0.101
	^{2}R (%)	99.79	97.81
Jovanovic	**q_m**	5.35	4.59
	K_J	0.0129	0.0157
	SSE	0.0011	0.0034
	^{2}R (%)	99.97	99.92

The values of R^2 are compared, Langmuir isotherm are shown to have higher values than Freundlich and Jovanovic isotherms. The lowest SSE values further confirmed the suitability of Langmuir model in describing the equilibrium data, suggesting the existence of monolayer adsorption of aspirin onto *Zizyphus Mauritiania* seeds and *Balanites Aegyptiaca* seeds. This result is consistent with the literature where it is reported that the adsorption of pharmaceutical products using various adsorbents is well represented by Langmuir isotherm model [27; 28]. The values of R_L, K_L and 1/n are in between zero and one give an indication of the favorability of the adsorption of aspirin onto biomaterials. It is interesting to note that the value of $K_L < 0.1$ is a sign of low surface energy, which indicates stronger bonding between aspirin and the adsorbents. The monolayer adsorption capacities were found to be 8.95 and 7.40 mg g^{-1} at *Zizyphus Mauritiania seeds* and *Balanites Aegyptiaca* seeds, respectively. This shows that the low-cost agro forest waste *Zizyphus Mauritiania seeds* and *Balanites Aegyptiaca* seeds can be used as adsorbents for the removal of aspirin from its aqueous solution. A list showing the adsorption capacity of different low-cost adsorbents for the adsorption of different pharmaceutical products materials from their aqueous solutions is given in Table 4.

Table 4. Adsorption capacities of different adsorbents for the uptake of different pharmaceutical products from their aqueous solutions

Adsorbent	Adsorbate	q_m (mg g^{-1})	References
Sugar Can Bagasse	Paracetamol	0.12	[14]
Vegetable Sponge		0.037	
Grape Stalk	Paracetamol	1.74	[15]
Yonimbe Bark		0.77	
Cork Bark		0.99	
Posidonia Oceanica	Paracetamol	1.638	[16]
Dehydrated Sewage Sludge		0.956	
Banana peel	Aspirin	2.29	[17]
Grape stalk	Caffeine	0.938	[18]
Zizyphus Mauritiana seeds	Caffeine	2.38	[19]
Balaanites Aegyptiaca seeds	Caffeine	4.28	[20]
Groundnut Shell	Paracetamol	3.02	[21]
Zizyphus Mauritiana seeds	Aspirin	8.95	Present study
Balaanites Aegyptiaca seeds	Aspirin	7.40	Present study

From Table 4, it is observed that the adsorption capacities of *Zizyphus Mauritiania* seeds and *Balanites Aegyptiaca* seeds as adsorbents for pharmaceutical product uptake are superior with other low cost adsorbents. The *Zizyphus Mauritiania* seeds and *Balanites Aegyptiaca* seeds without any treatment applied in this work can be considered promising biomaterials to be used for aspirin adsorption. Previous works confirms the importance of *Zizyphus Mauritiania* seeds and *Balanites Aegyptiaca* seeds in water decontamination [29-32].

Conclusion

The equilibrium adsorption of aspirin by *Zizyphus Mauritiania* seeds and *Balanites Aegyptiaca* seeds as low cost adsorbents was explained using the Langmuir, Freundlich and Jovanovic isotherms. The present study showed that the adsorption of aspirin by all two biomaterials was found to be well represented by Langmuir. The monolayer adsorption capacities were found to be 8.95 and 7.40 mg g^{-1} at *Zizyphus Mauritiania* seeds and *Balanites Aegyptiaca* seeds, respectively. These results showed that the *Zizyphus Mauritiania* seeds and *Balanites Aegyptiaca* seeds without any treatment can be considered promising biomaterials to be used for pharmaceutical products adsorption.

For future studies, the usability of *Zizyphus Mauritiania* seeds and *Balanites Aegyptiaca* seeds for pharmaceutical products removal from real wastewater will be tested and as comparison, a fixed bed column will be employed to investigate the effect of reactor design.

References

1. S.D. Kim, J. Cho, I.S. Kim, B.J. Vanderford, S.A. Snyder. Occurence and Removal of Pharmaceuticals and Endocrine Disruptors in South Korean Surface, Drinking, and Wastewaters. *Water Research*. 41 (2007) 1013-1021
2. C. Zwiener, Occurrence and Analysis of Pharmaceuticals and Their Transformation Products in Drinking Water Treatment. *Analytical and Bioanalytical Chemistry*. 387(4) (2007) 1159-1162.
3. M.J. Benotti, R.A. Trenholm, B.J. Vanderford, J.C. Holady, B.D. Stanford, S.A. Snyder, Pharmaceuticals and Endocrine Disrupting Compounds in Us Drinking Water. *Environmental Science & Technology*. 43(3) (2008) 597-603.
4. S. Mompelat, B. Le Bot, O. Thomas, Occurrence and Fate of Pharmaceutical Products and by-Products, from Resource to Drinking Water. *Environment international* 35(5) (2009) 803-814.
5. W.J. Sim, J.W. Lee, J.E. Oh, Occurrence and Fate of Pharmaceuticals in Wastewater Treatment Plants and Rivers in Korea. *Environmental Pollution*. 158, (5) (2010) 1938-1947.
6. S.L. Bartelt-Hunt, D.D. Snow, T. Damon, J. Shockley, H. Hoagland, The occurrence of illicit and therapeutic pharmaceuticals in wastewater effluent and surface waters in Nebraska. *Environ Pollut.*, 157 (2009) 786-791.
7. C. Carrara, C.J. Ptacek, W.D. Robertson, D.W. Blowes, M.C. Moncur, Ed Sverko, Sean Backus, Fate of pharmaceutical and trace organic compounds in three septic system plumes, Ontario, Canada. *Environ. Sci. Technol*., 42 (2008) 2805-2811. https://doi.org/10.1021/es070344q
8. A. Azman, N. Ngadi, D.K.A. Zaini, M. Jusoh, Z. Mohamad, A. Arsad, Effect of Adsorption Parameter on the Removal of Aspirin Using Tyre Waste Adsorbent; *Chemical Engineering Transactions*, 72 (2019) 157-162
9. R. Broséus, S. Vincent, K. Aboulfadl, A. Daneshvar, S. Sauvé, B. Barbeau, M. Prévost, Ozone oxidation of pharmaceuticals, endocrine disruptors and pesticides during drinking water treatment, *Water research*, 43 (2009) 4707-4717.
10. C. Cruz-Morató, D. Lucas, M. Llorca, S. Rodriguez-Mozaz, M. Gorga, M. Petrovic, D. Barceló, T. Vicent, M. Sarrà, E. Marco-Urrea, Hospital wastewater treatment by fungal bioreactor: removal efficiency for pharmaceuticals and endocrine disruptor compounds, *Science of the Total Environment*, 493 (2014) 365-376.
11. J. Radjenović, M. Petrović, F. Ventura, D. Barceló, Rejection of pharmaceuticals in nanofiltration and reverse osmosis membrane drinking water treatment, *Water Research*, 42 (2008) 3601-3610.
12. A.D. N'diaye, M. Kankou, Sorption of Aspirin from Aqueous Solutions using Rice Husk as Low Cost Sorbent, *Journal of Environmental Treatment Techniques*, 8(1) (2020) 1-5
13. A. D. N'diaye, Modeling of adsorption isotherms of dyes onto various adsorbents: A Short Review *Arab. J. Chem. Environ. Res.* 05 (2018) 42-51
14. A.V.F.N. Ribeiro, M. Belisário, R.M. Galazzi, D.C. Balthazar, M. Godoi Pereir, J.N. Ribeiro, *Electronic Journal of Biotechnology*, 14 (2011) 6
15. I. Villaescusa, N. Fiol, J. Poch, A. Bianchi, C. Bazzicalupi, Mechanism of paracetamol removal by vegetable wastes: The contribution of π–π interactions, hydrogen bonding and hydrophobic effect, *Desalination*, 270, (1–3) (2011)135 142.
16. M. Ferchichi, H. Dhaouadi, Sorption of paracetamol onto biomaterials, *Water Science and Technology*, 74, (1) (2016) 287–294.
17. A.V.F.N. Ribeiro, A.R. Da Silva, T.P. Ca Cunha, R.T.L. Dos Santos, J.P. De Oliveira, E.V. Pereira, M.V.V.J. Licinio, M. De Godoi Pereira, A.V. Dos Santos, J.N. Ribeiro, Banana Peel for Acetylsalicylic Acid Retention. *Journal of Environmental Protection*, 7 (2016) 1850-1859

18. R. Portinho, O. Zanella, L.A. Féris, Grape stalk application for caffeine removal through adsorption. *Journal of Environmental Management*, 202 (2017) 178–187
19. A.D. N'diaye, M.S.A. Kankou, Sorption of caffeine onto low cost sorbent: Application of two and three-parameter isotherm models, *Applied Journal of Environmental Engineering Science* 5, 3 (2019) 263-272
20. A.D. N'diaye, M.S.A. Kankou, Valorization of *Balanites aegyptiaca* seeds from Mauritania: Modeling of adsorption isotherms of caffeine from aqueous solution, *Journal of Environmental Treatment Techniques*, 7, 3 (2019) 450-455;
21. A.D. N'diaye, M.A. Bollahi, M.S.A. Kankou, Sorption of paracetamol from aqueous solution using groundnut shell as a low cost sorbent, *J. Mater. Environ. Sci.* 10 (6) (2019) 553-562
22. M.I. El-Khaiary, Least-squares regression of adsorption equilibrium data: comparing the options, J. Hazard. Mater. 158 (2008) 73–87.
23. G. Thompson, J. Swain, M. Kay, C.F. Forster, The treatmentof pulp and paper mill effluent: a review, Bioresour. Technol. 77 (2001) 275–286.
24. I. Langmuir, The constitution and fundamental properties of solids and liquids. Part I. Solids. *Journal of the American Chemical Society*, 1916, 38, (11) (1916) 2221–2295
25. D.S. Jovanović, Physical adsorption of gases. *Kolloid-Zeitschrift & Zeitschrift Für Polymere*, 235(1) (1969) 1214–1225
26. H. Freundlich, Adsorption in solution. *Z. Phys. Chemie*., 57 (1906) 384-470.
27. M. Galhetas, A.S. Mestre, M.L. Pinto, I. Gulyurtlu, H. Lopes, A.P. Carvalho, Chars from gasification of coal and pine activated with K_2CO_3: acetaminophen and caffeine adsorption from aqueous solutions. *J. Colloid Interface Sci*. 433 (2014) 94-103.
28. V.M. Nurchi, M. Crespo-Alonso, M.I. Pilo, N. Spano, G. Sanna, R. Toniolo, Sorption of ofloxacin and chrysoidine by grape stalk. A representative case of biomass removal of emerging pollutants from wastewater, *Arab. J. Chem*. 12 (2019) 1141-1147. doi.org/10.1016/j.arabjc.2015.01.006.
29. M. Najem, H. Maauof, M. Erhayem, M. Farj, Removal of Methylene Blue Dye from Aqueous Solution Using Activated seed shell of Balanites Aegyptiaca L Delile, *Journal of Pure & Applied Sciences (JOPAS)*, 18(3) (2019) 13-17
30. G. Wyasu, C.E. Gimba, E.B. Agbaji, G.I. Ndukwe Production and Characterization of Active Carbon from Epicarp of Balanite aegyptiaca and Detarium mirocarpum Shells, *Int. J. Sci. Technoledge*, 4(3) (2016) 19-25
31. N. Boudechiche, M. Fares, S. Ouyahi, H. Yazid, M. Trari, Z. Sadaoui, Comparative study on removal of two basic dyes in aqueous medium by adsorption using activated carbon from Ziziphus lotus stones, *Microchemical Journal*, 146 (2019) 1010-1018, doi.org/10.1016/j.microc.2019.02.010
32. P. Mohebbi, M. Parvini, H.Z. Mousavi, Removal of erythrosine dyes from aquatic environment using Ziziphus nummularia kernel, *Iranica Int. J. Energy Environ.*, 5 (2014) 400-406, 10.5829/idosi.ijee.2014.05.04.08

(2020); http://www.jmaterenvironsci.com