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# Valorization of Balanites aegyptiaca Seeds from Mauritania: Modeling of Adsorption Isotherms of Caffeine from Aqueous Solution

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## Abstract

This paper focuses on the development and characterization of low cost sorbent to Balanites aegyptiaca seeds without treatment and its application in the adsorption of caffeine in aqueous solution. The Balanites aegyptiaca seeds were characterized by using physicochemical parameters, Scanning Electron Micrograph (SEM) and Fourier Transform Infra-Red spectroscopy (FTIR). Batch sorption experiments are intended to identify the adsorption isotherms of the caffeine on the Balanites aegyptiaca seeds. Four isotherm models (Freundlich, Langmuir, Redlich–Peterson and Sips) were tested for modeling the adsorption isotherms by nonlinear method. The maximum adsorption capacity was found to be 4.28 mg $g^{-1}$. Based on data obtained in this study, it can be concluded that the Balanites aegyptiaca seeds are a promising sorbent.

**Keywords**: Balanites aegyptiaca seeds, sorbent, caffeine, nonlinear, isotherms

## 1 Introduction

Caffeine ($C_8H_{10}N_4O_2$) (figure 1) is one of the most consumed stimulating substances [1]. Caffeine has a high water solubility and low octanol–water partition coefficient [2; 3]. Due to the low efficiency of conventional wastewater treatment process, caffeine has been detected in many surface water and ground water [4; 5].

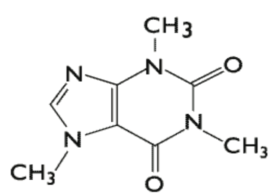

Figure 1: Molecular structure of caffeine

Some treatment technologies are introduced to remove caffeine from water and wastewater, including electrochemical degradation [6], ultrafiltration [7], membrane treatment [8] and electro coagulation [9]. However, most of these methods suffer from some disadvantages such as the high cost, the low efficiency, and high energy consumption limit the wide application of these technologies.

In recent years, immense research has been focused towards valorization of agricultural or industrial wastes for their uses in the water and wastewater treatment consequently; this strategy reduces the treatment cost and contributes to ecofriendly development. The adsorption is considered as promising and an interesting alternative to operate mainly using biomaterials [10-15].

Balanites aegyptiaca is a tree native to Africa and the Middle East and all parts of the plant are used in traditional medicine [16]. In this research, the cheapest and abundantly available in Mauritania aegyptiaca balanites seeds have been used as adsorbent to remove caffeine from aqueous solution.

Several techniques were performed to characterize the Balanites aegyptiaca seeds such as physicochemical parameters, Scanning Electron Micrograph (SEM) and Fourier Transform Infra-Red spectroscopy (FTIR). The retention capacity of caffeine onto the Balanites aegyptiaca seeds is investigated with using the non-linear parameter equation of Langmuir, Freundlich, Sips and Redlich – Peterson isotherm models.

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## 2 Materials and methods

### *2.1 Caffeine solutions*

Caffeine, in analytical purity and used in the experiments directly. The caffeine solutions were prepared by diluting stocks solution to appropriate concentrations when needed.

### *2.2 Sorbent and experimental procedures*

The used Balanites aegyptiaca seeds (Figure 2) were collected from the south of Mauritania. The Balanites aegyptiaca seeds were washed thoroughly with ultra pure water and sundried for 5 days. After, the seeds are broken and were ground and sieved to obtain particle sizes below 100 µm, dried in an oven at 105 °C for 24 h and stored in a dessicator before use.

Figure 2: Balanites aegyptiaca seeds

The pH of the Balanites aegyptiaca adsorbent was carried out according to Abdel-Halim et al (2006) [17]. The physicochemical parameters like the moisture, volatile matter and ash are determined by described methods [18]. The determination of cellulose, lignin and hemicellulose in Balanites aegyptiaca seeds were analyzed by the procedure indicated by Li et al (2004) [19]. The morphology of the Balanites aegyptiaca seeds adsorbent was determined using SEM. The Balanites aegyptiaca seeds were analyzed by the FTIR spectroscopy to determine the surface functional groups. The wavenumber scanning is in the range of 650–4,000 cm$^{-1}$.

The sorption isotherms at ambient temperature are obtained by mixing (70 rpm), for 6 hours, 0.5 g of Balanites aegyptiaca seeds with 50 mL of caffeine solutions with different concentrations varying from 10 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 caffeine was determined by High Performance Liquid Chromatography (HPLC). Ultra pure water and methanol (70:30 V/V) were used as a mobile phase at a flow rate of 1 mL min$^{-1}$ at a selected wave length of 254 nm. Ambient temperature (25 °C), pH (7.2) and all experimental parameters are constant throughout the various tests. The caffeine uptake amount $q_e$ (mg of caffeine per g of dried Balanites aegyptiaca seeds sorbent) was calculated using the equation (1):

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

where $q_e$ is quantity of caffeine per g of Balanites aegyptiaca seeds (mg g$^{-1}$), $C_i$ is initial solution concentration of caffeine (mg L$^{-1}$), $C_e$ is equilibrium solution concentration of caffeine (mg L$^{-1}$), m is the Balanites aegyptiaca seeds weight (g), and V is volume of the solution (L).

### *2.3 Equilibrium studies*

Several isotherm equations can explain solid–liquid adsorption systems, such as: Langmuir, Freundlich, Sips and Redlich-Peterson. The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogeneous surface sites within the adsorbent and has found successful application in many sorption processes of monolayer adsorption. The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems [20]. The Sips isotherm is a combination of the Langmuir and Freundlich isotherms, which represent systems for which one adsorbed molecule could occupy more than one adsorption site [21]. The Redlich–Peterson isotherm model combines elements from both the Langmuir and Freundlich equation and the mechanism of adsorption is a hybrid one and does not follow ideal monolayer adsorption. It is used as a compromise to improve the fit by Langmuir or Freundlich equation. The exponent “n” ranges between 0 and 1. For n = 1, Redlich–Peterson equation leads to Langmuir one [22]. All the used mathematical models for caffeine adsorption isotherm are shown in Table 1.

Table 1: Mathematical models for sorption isotherms

| Isotherm | Equation | Parameter (dimension) |
|---|---|---|
| Langmuir | $q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$ | $q_m$ (mg g$^{-1}$)<br>$K_L$ (mg L$^{-1}$)$^{-1}$ |
| Freundlich | $q_e = K_F C_e^{1/n}$ | $K_F$ (mg/g) × (mg/L)$^{-n}$<br>n |
| Sips | $q_e = q_m \frac{K_S C_e^n}{(1 + K_S C_e^n)}$ | $q_m$ (mg g$^{-1}$)<br>$K_S$ constant (L mg−1)$^m$<br>n |
| Redlich-Peterson | $q_e = \frac{K_{RP} C_e}{1 + \alpha_{RP} C_e^n}$ | $K_{RP}$ (mg/g)×(mg/L)$^{n-1}$<br>$\alpha_{RP}$<br>n |

The correlation coefficient $R^2$, the Sum of the Squares of the Errors (SSE) and Chi-square ($\chi^2$) analysis is used to fit experimental data with isotherm using the Excel® solver. The correlation coefficient $R^2$, SSE and $\chi^2$ values are determined respectively by following equations (2), (3) and (4):

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

$$SSE = \left(q_{exp} - q_{mod}\right)^2 \quad (3)$$

$$\chi^2 = \sum\left(\left(q_{exp} - q_{mod}\right)^2 / q_{mod}\right) \quad (4)$$

where $q_{exp}$ (mg $g^{-1}$) is equilibrium capacity from the experimental data, $q_{avr}$ is equilibrium average capacity from the experimental data and $q_{mod}$ 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 discussions

### *3.1 Characterization of aegyptiaca balanites seeds*

The physicochemical properties of the Balanites aegyptiaca seeds adsorbent are shown in table 2. The pH of the aegyptiaca balanites seeds was found to be 6.12. From the proximate analysis, it was observed that moisture, ash, volatile matter 3.9 %, 5.7 % and 78.2 %, respectively. The cellulose, hemicellulose and lignin values of the Balanites aegyptiaca seeds, depending on soil properties and the plant's development stage, are 41.3, 33.9 % and 15.2 % respectively.

Table 2: Characterization of aegyptiaca balanites seeds

| parameters | values |
|---|---|
| pH | 6.12 |
| Moisture (%) | 3.9 |
| Ash (%) | 5.7 |
| Volatile matter (%) | 78.2 |
| Hémicellulose (%) | 33.9 |
| Cellulose (%) | 41.3 |
| Lignin (%) | 15.2 |

The FTIR spectroscopy analyses of the Aegyptiaca Balanites seeds are given in figure 3. FTIR spectra for the Aegyptiaca Balanites seeds displayed a number of peaks pertaining to different functional groups. O–H stretching of the hydroxyl of the alcohols groups and bonded hydroxyl groups of cellulose: 3054.76 $cm^{-1}$. The peak at 2987.39 $cm^{-1}$ was assigned to C–H asymmetrical stretching of methyl groups on the surface of Balanites aegyptiaca seeds adsorbent. These groups were present on the lignin structure. The peak located at 1732.61 $cm^{-1}$ was characteristics of the carbonyl group stretching from carboxylic acids and ketones. The peak at 1421.93 $cm^{-1}$ was attributed to the stretch vibration of C–O from the carboxyl group. The peak at 1264.37 $cm^{-1}$ was due to the asymmetric bending vibration of the $-CH_3$ group. The wave number observed at 1029.36 $cm^{-1}$ was due to the C-O group in carboxylic and alcoholic groups and shows the presence of Si-O-Si linkages. The analysis of the FTIR spectrum showed the presence of carboxyl and hydroxyl, these functional groups may be the major biosorption sites for caffeine removal. SEM slides of Balanites aegyptiaca seeds (figure 4) revealed a stick shape of the prepared powder with a predominance of white spots (corresponding to silica, a like grafted component), on Balanites aegyptiaca seeds surface as confirmed by FTIR analysis.

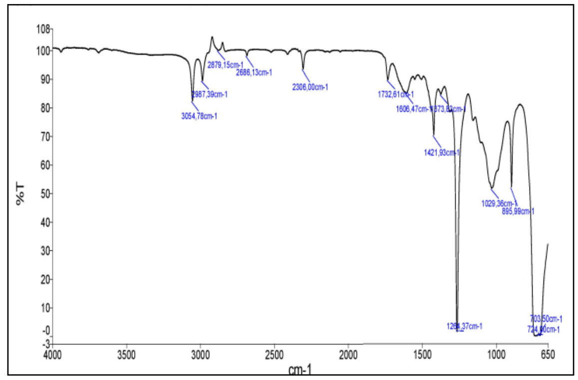
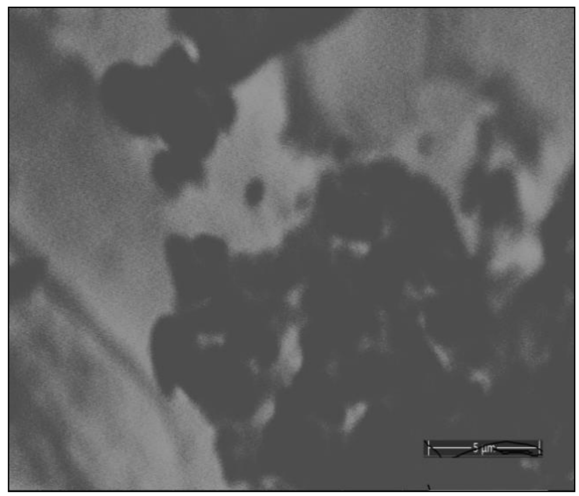
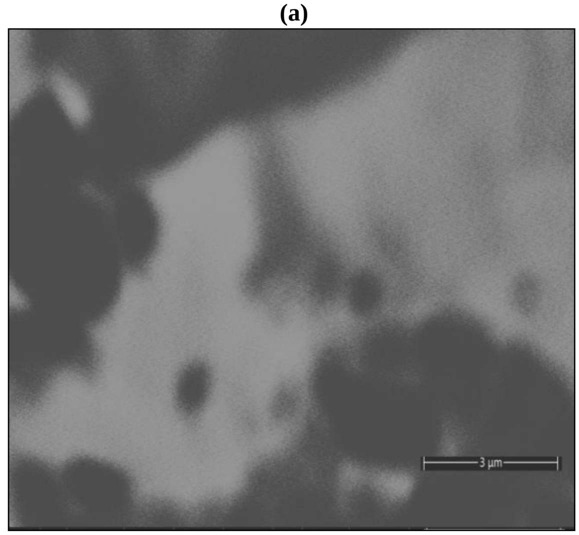



Figure 3: FTIR Spectrum of balanites aegyptiaca seeds



**(a)**



**(b)**

Figure 4: Scanning electron microscopy images for the Balanites aegyptiaca seeds sample magnified (a) ×5000 and (b) ×10000

### *3.2 Adsorption equilibrium isotherms determination*

Adsorption isotherms were analyzed according to the nonlinear form of Langmuir, Freundlich, Redlich–Peterson and Sips isotherms. The non linear method does not transform data sets; hence, no distortions are created in the original error distribution. Comparisons of linear and nonlinear regressions often concluded that the best parameter estimates were returned by nonlinear optimizations [23-25]. Equilibrium times between 2 and 4 h are reported for caffeine adsorption onto activated carbon [12; 26; 27]. Even so, Torrelas et al (2015) [27] highlight most of the adsorption process occurs in the first 5 min. Equilibrium time of 60 min is reported for caffeine adsorption onto Grape stalk, grape stalk modified by phosphoric acid and grape stalk activated carbon [13]. In our study, residence time selected was 6 h for Balanites aegyptiaca seeds adsorbent in order to optimize experiments duration without significant losses in adsorption capacities.

The three-parameter model, Langmuir and Freundlich have been applied to evaluate the fit by isotherm for the adsorption of caffeine onto Balanites aegyptiaca seeds by figure 5. According to Table 3, the coefficients of correlation are very good ($R^2 \geq 97.8$ %), lower values of SSE and good $\chi^2$ for both models. The values of $K_L$ and $1/n_F$ are less than unity indicating that the caffeine is favorably adsorbed by the Balanites aegyptiaca seeds.

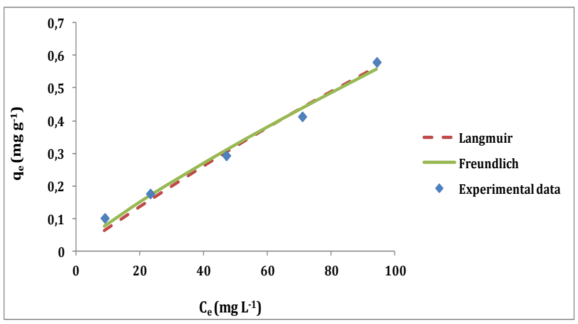



Figure 5: Two- parameters isotherms obtained using the non-linear method for the sorption of caffeine onto Balanites aegyptiaca seeds

Table 3: Two-isotherm parameters for caffeine onto Balanites aegyptiaca seeds

| Langmuir | Freundlich |
|---|---|
| $q_m$=4.28 | $1/n_F$=0.85 |
| $K_L$=0.0016 | $K_F$=0.012 |
| $R^2$(%)=97.8 | $R^2$ (%)=98.5 |
| SSE=0.0031 | SSE=0.0021 |
| $\chi^2$ =0.0322 | $\chi^2$ =0.0126 |

Among the tested three-parameter equations, the better and perfect representation of the experimental results of the adsorption isotherms is obtained using the Redlich-Peterson model (figure 6). According to Table 4, the coefficients of correlation are very good (≥99.5), lower values of SSE and good $\chi^2$ for the both models. It was reported that $n_{RP}$ is considered a measure of the adsorption affinity [28]. According the table 4, it is clear that $n_{RP}$ value approaches unity (0.77), indicated that the sorption data were more of Langmuir isotherm. It can be concluded that surface of Balanites aegyptiaca seeds homogenous for caffeine adsorption. The Sips isotherm suggests that the sorption capacity of Balanites aegyptiaca seeds to uptake caffeine to be 0.066 mg $g^{-1}$. The maximum adsorption capacity predicted by the Sips isotherm was lower than Langmuir isotherm.

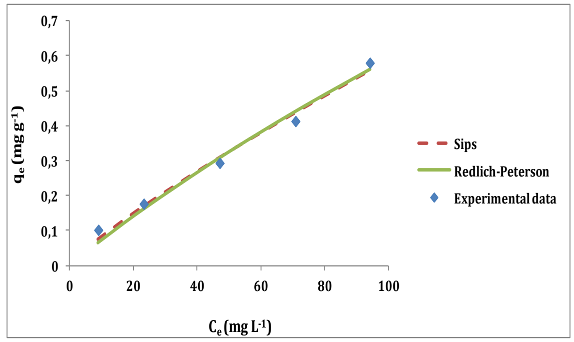



Figure 6: Three- parameters isotherms obtained using the non-linear method for the sorption of caffeine onto Balanites aegyptiaca seeds

Table 4: Three-isotherm parameters for caffeine onto Balanites aegyptiaca seeds

| Sips | Redlich-Peterson |
|---|---|
| $q_m$=0.066 | $K_{RP}$=0.0076 |
| $K_S$=0.29 | $\alpha_{RP}$=0.0081 |
| $n_S$=0.85 | $n_{RP}$=0.77 |
| $R^2$ (%)=98.5 | $R^2$ (%)=99.5 |
| SSE=0.0021 | SSE=0.0029 |
| $\chi^2$ =0.0127 | $\chi^2$ =0.0251 |

Although the values of adsorption capacity $q_m$ for Balanites aegyptiaca seeds on caffeine removal are still smaller than the capacities of activated carbons and others treated materials [10;12-15], the Balanites aegyptiaca seeds without any treatment applied in this work can be considered a promising material to be used for caffeine adsorption. We can say that for to improve the retention capacity of caffeine from water and wastewater, the setting up of activation processes of the Balanites aegyptiaca seeds is necessary.

## 4 Conclusions

In this paper, the low cost adsorbent was prepared from Balanites aegyptiaca seeds, without any treatment. The prepared adsorbent were characterized by determining different parameter such as pH, moisture content, ash content, volatile matter, cellulose, hemicellulose, lignin, SEM and FTIR spectroscopy. The equilibrium isotherm data obtained during sorption of caffeine onto Balanites aegyptiaca seeds were fitted using different two and three-parameter models with using the non linear method.

The isotherm data can well be fitted with Langmuir and Redlich–Peterson models. The maximum adsorption capacity was found to be 4.28 mg $g^{-1}$, compared with the adsorption capacities obtained by activated carbons and others treated materials for sorption of caffeine show that the Balanites aegyptiaca seeds are cheap and economically suitable for removal of caffeine from water and wastewater.

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