

Sorption of paracetamol from aqueous solution using groundnut shell as a low cost sorbent

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Abstract

In this study, the sorption of paracetamol on groundnut shell as low cost sorbent was investigated using the batch equilibrium method. Physicochemical parameters, X-ray Fluorescence and Fourier Transform Infra-Red (FTIR) Spectroscopy were used for groundnut shell characterization. Equilibrium studies were carried out for the sorption of paracetamol from aqueous solution onto groundnut shell. The experimental data were fitted to the two-parameter isotherms (Langmuir, Freundlich and Temkin) and three-parameter isotherms (Sips, Redlich – Peterson and Toth). 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. Among two-parameter models, the Langmuir better described the isotherm data. The retention of paracetamol on the groundnut shell showed a relatively significant sorption with a maximal quantity of 3.02 mg.g^{-1} . From three-parameter isotherms, Sips model was found to be the best representative for paracetamol sorption on the groundnut shell. The present study showed that the powdered groundnut shell is a promising and alternative sorbent for the removal of paracetamol from aqueous solution.

1. Introduction

The frequent contamination of water resources with pharmaceutical products antibiotics, hormones, analgesics, psychotropics, antipyretics and anti-inflammatories has attracted enormous attention because of their residues will then reach aquatic environment via wastewater treatment plants (WWTPs) [1-3]. Due to the low efficiency of conventional wastewater treatment process, pharmaceutical residues have been detected in surface water, ground water and mineral waters [4-6]. The presence of these pharmaceuticals in the environment poses the threat to aquatic organisms in terms of mutagenicity as well as currently unknown effects to humans [7].

Among those, paracetamol which molecular structure is represented in Figure 1 is one of the most commonly prescribed pharmaceutical drugs as in analgesic and antipyretic therapy. This compound reaches the natural environment either through direct disposal of domestic drugs, discharges of feces/urine or the inappropriate treatment of industrial effluents [8].

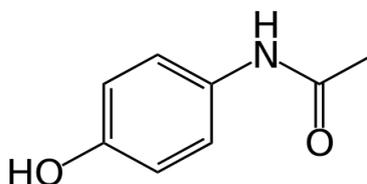


Figure 1: Molecular structure of paracetamol

Some methods have been applied for the elimination of paracetamol such as microbiological [9; 10], electrochemical [11], nanofiltration and reverse osmosis [12], ultrafiltration [13], ozone and biofiltration [14], photocatalytic [15], degradation by Fenton oxidation [16], bioelectrochemical [17] and adsorption [18].

Solid-phase adsorption is one of the most efficient technologies for the treatment of pharmaceutical products in water. The adsorption of paracetamol onto activated carbons has attracted many researchers, but its high cost inhibits its application on a large scale [19; 20].

In order to overcome this problem, we have used the agricultural waste material for the removal of paracetamol from aqueous solution. A groundnut shell is often considered as solid waste of agriculture. Groundnut is cultivated in over 100 nations around the world. Main producers are China and India, which are providing more than 60 % of the production. Africa realizes 25 % of the production, thanks mainly to Nigeria, Senegal and Sudan [21].

In this research, the cheapest and unconventional groundnut shell has been used as low cost sorbent to remove paracetamol from aqueous solution. Physicochemical parameters, X-ray Fluorescence and Fourier Transform Infra-Red (FTIR) Spectroscopy were used for groundnut shell characterization. The retention capacity of paracetamol onto the groundnut shell is investigated with using the non-linear two-parameter models (Langmuir, Freundlich and Temkin) and non-linear three-parameter models (Sips, Redlich –Peterson and Toth).

2. Material and Methods

2.1. Paracetamol solutions

All the solutions are prepared using pure paracetamol and ultra-pure water. The stock solution is prepared by adding 1 g of the active ingredient to 1L of ultrapure water. Other concentrations are prepared by dilutions of the stock solution and used to develop the standard curves. The physicochemical properties of paracetamol are given in Table 1 [18].

Table 1: Physicochemical properties of paracetamol

Molecular weight (g mol ⁻¹)	Log K _{ow}	pKa	Water solubility (g L ⁻¹)
151.16	0.46	9.38	12.9

2.2. Preparation and characterization of groundnut shell

The used groundnut shell (Figure 2) was collected from the local market of Nouakchott City in Mauritania. Before use, the groundnut shell was washed thoroughly with ultra pure water to remove adhered soil and dust and sundried for 8 hours. The dried shell was ground to powder, sieved to obtain particle sizes below 100 µm, dried in an oven at 80°C for 24 hours and stored in a dessicator before use.



Figure 2: collected groundnut shell

The point of zero charge (pH_{pzc}) of the groundnut shell was carried out [22]. The physicochemical parameters like the moisture, volatile matter and ash are determined by described methods [23]. The bulk density was determined using a picnometer [24].

The metal oxides of groundnut shell were analyzed using X-ray fluorescence. Different samples of groundnut shell were analyzed by the Fourier Transform Infra- Red (FTIR) Spectroscopy to determine the surface functional groups in the scanned range of 650–4,000 cm⁻¹.

2.3. Adsorption isotherms

The adsorption isotherms are obtained by mixing (70 rpm), for 12 hours, 0.5 g of groundnut shell with 25 mL of paracetamol solutions with different concentrations varying from 10 to 100 mg L⁻¹. At the end of each experiment the agitated solution mixture was microfiltered using micro filter and the residual concentration of paracetamol 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, pH (6.8) and all experimental parameters are constant throughout the various tests. The adsorbed quantity at equilibrium (q_e) is calculated according to the following equation (1):

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

Where

- q_e : quantity of paracetamol per g of groundnut shell (mg.g⁻¹),
- C_i : initial solution concentration of paracetamol (mg L⁻¹),
- C_e : equilibrium solution concentration of paracetamol (mg L⁻¹),
- m : the groundnut shell weight (g),
- V : Volume of the solution (L).

Adsorption isotherms play an important role in the determination of the maximum adsorption capacity and the identification of the type of adsorption to occur. Several isotherm equations can explain solid-liquid adsorption systems, such as: Langmuir, Freundlich, Temkin, Sips, Redlich-Peterson and Toth.

The Langmuir adsorption isotherm assumes that the adsorption takes place at specific homogeneous surface sites within the sorbent and has found successful application in many adsorption processes of monolayer adsorption [25; 26]. The nonlinear Langmuir model can be expressed by equation (2):

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

Where q_e is the amount of paracetamol sorbed per unit mass of groundnut shell (mg.g⁻¹), k_L is the Langmuir constant related to the sorption capacity (L g⁻¹), C_e is the concentration of paracetamol in the solution at equilibrium (mg L⁻¹), q_m is the maximum uptake per unit mass of groundnut shell (mg.g⁻¹). The factor of separation of Langmuir, R_L , which is an essential factor characteristic of this isotherm is calculated by using the relation (3) [27]:

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

Where C_0 is the higher initial concentration of paracetamol, while K_L and q_m is the Langmuir constant and the maximum sorption capacity, respectively. The parameters indicate the shape of the isotherm as follows: R_L values indicate the type of isotherm. The R_L value implies the sorption to be defavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$), or irreversible ($R_L = 0$).

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. It assumes neither homogeneous site energies nor limited levels of sorption [25; 26]. The nonlinear representation of the Freundlich model is as in equation (4):

$$q_e = K_F C_e^{1/n} \quad (4)$$

Where K_F (mg.g⁻¹) (L mg⁻¹)ⁿ and $1/n$ are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

The Temkin isotherm assumes that the fall in the heat of adsorption is linear rather than logarithmic, as implied in the Freundlich equation. The heat of sorption of all the molecules in the layer would decrease linearly with coverage due to sorbate/sorbent interactions [28]. The Temkin isotherm has generally been applied in the following non linear form (5):

$$q_e = B_1 \ln K_T C_e \quad (5)$$

Where $B_1 = RT/b$ is a constant related to heat of sorption and b shows the variation of adsorption energy (J mol^{-1}). K_T is a Temkin constant which take onto account the interactions sorbate/sorbent ($\text{dm}^3 \text{mg}^{-1}$). 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 [29]. The nonlinear representation of the Sips model is as in equation (6):

$$q_e = q_m \frac{K_S C_e^n}{(1 + K_S C_e^n)} \quad (6)$$

Where q_m the Sips maximum adsorption capacity (mg.g^{-1}), K_S the Sips equilibrium constant (L mg^{-1}) and n the Sips model exponent describing heterogeneity.

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 [30]. The nonlinear representation of the Redlich–Peterson model is as in equation (7):

$$q_e = \frac{K_{RP} C_e}{1 + \alpha_{RP} C_e^n} \quad (7)$$

Where K_{RP} (L g^{-1}) and α_{RP} (L mol^{-1}) are the Redlich-Peterson isotherm constants, while n is the exponent, which lies between 0 and 1.

The Toth isotherm model combines the characteristics of both the Langmuir and Freundlich isotherm. It approaches the Freundlich model at high concentration and is in agreement with the low concentration limit of the Langmuir equation [30]. The nonlinear representation of the Toth model is as in equation (8):

$$q_e = q_m \frac{C_e}{(1 + \alpha_T C_e)^{1/n}} \quad (8)$$

Where q_m the Toth maximum adsorption capacity (mg.g^{-1}), α_T is adsorptive potential constant (mg L^{-1}) and n Toth's heterogeneity factor.

To optimize the design of an adsorption system for the removal of paracetamol, it is important to establish the most appropriate correlation for the equilibrium data. The relative parameters of each equation are obtained using Sum of the Squares of the Errors (SSE) and the correlation coefficient R^2 between the calculated data and the experimental data by nonlinear method analysis [31; 32]. The SSE and R^2 values, by using the Solver Excel, are determined respectively by following equations (9) and (10):

$$\text{SSE} = (q_{\text{exp}} - q_{\text{mod}})^2 \quad (9)$$

$$R^2 = 100 \left(1 - \frac{\|q_{\text{exp}} - q_{\text{mod}}\|^2}{\|q_{\text{exp}} - q_{\text{avr}}\|^2} \right) \quad (10)$$

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

3.1. Characterization of groundnut shell

The results of physicochemical characteristics of the groundnut shell as obtained in this work are shown in Table 2.

The pH_{pzc} of the groundnut shell was found to be 5.8. As regards the surface chemistry the value of the pH_{pzc} revealed that the studied groundnut shell possess predominantly acidic nature. The bulk density was found to be 0.57 g mL^{-1} .

From the proximate analysis, it was observed that moisture, ash and volatile matter was slightly high which may be due to its plant origin [33].

Table 2: physicochemical characteristics of groundnut shell

Parameters	Mean
pH_{pzc}	5.8±0.10
Moisture (%)	4.7±0.36
Ash (%)	2.7±0.17
Volatile matter (%)	67.1±1.57
Bulk density (g mL ⁻¹)	0.57±0.03
Particle size (µm)	< 100

Table 3 gives some results of metal oxides of the groundnut shell which was determined by X-ray fluorescence. The results show that the potassium, calcium, magnesium and silica oxides are major component of the groundnut shell. The X-ray fluorescence results show the presence of constituents such as K₂O (67.7 g.kg⁻¹), CaO (48.4 g.kg⁻¹) and P₂O₅ (3.6 g.kg⁻¹) in groundnut shell, which act as micronutrients to the soil according to [34]. Other associated oxides such Al₂O₃, Fe₂O₃, Na₂O, MnO, P₂O₅, SO₃ and TiO₂ are present with very low percentages. However, some trace metals such as V, Cr, Sr, Zr, Ba, Ni, Cu, Zn and Pb were not detected by X-ray fluorescence.

Table 3: Chemical composition of groundnut shell (wt %)

Compound	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	MnO	P ₂ O ₅	SO ₃	TiO ₂
wt. (%)	0.44	2.1	0.2	1.38	4.84	≤ 0.01	6.77	0.05	0.36	≤ 0.01	0.05

The FTIR spectroscopy analysis of the groundnut shell before and after paracetamol sorption is given in Figures 3a and 3b, respectively. The FTIR spectra of the sorbent before paracetamol retention are used as a reference for interpreting any possible structural changes.

The presence of a broad peak at 3337.33 cm⁻¹ representing surface bonded O-H groups linked in cellulose, lignin, adsorbed water or a stretching N-H group [35; 36]. The peak at 2920.30 cm⁻¹ is attributed to the symmetric and asymmetric C-H stretching vibration of aliphatic acids. The absorption band at 1607.24 cm⁻¹ is characteristic of C=O stretching vibrations of ketones, aldehydes, lactones, or carboxyl groups [37]. This peak also was shifted to 1630.99 cm⁻¹. The vibration band of C=C at 1420.75 cm⁻¹ disappears after paracetamol sorption. The wave number observed at 1026.86 cm⁻¹ shows the presence of O-Si-O linkage. This peak also shifted to 1031.86 cm⁻¹ after paracetamol sorption. The presence of O-Si-O is confirmed by X-ray fluorescence (see Table 3).

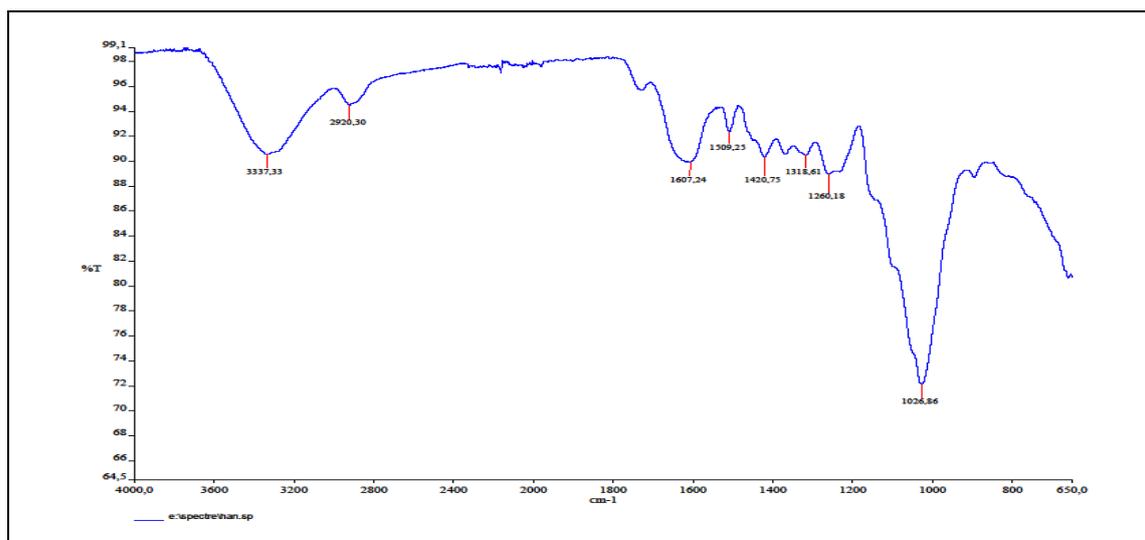


Figure 3a: FTIR Spectrum of groundnut shell before paracetamol sorption

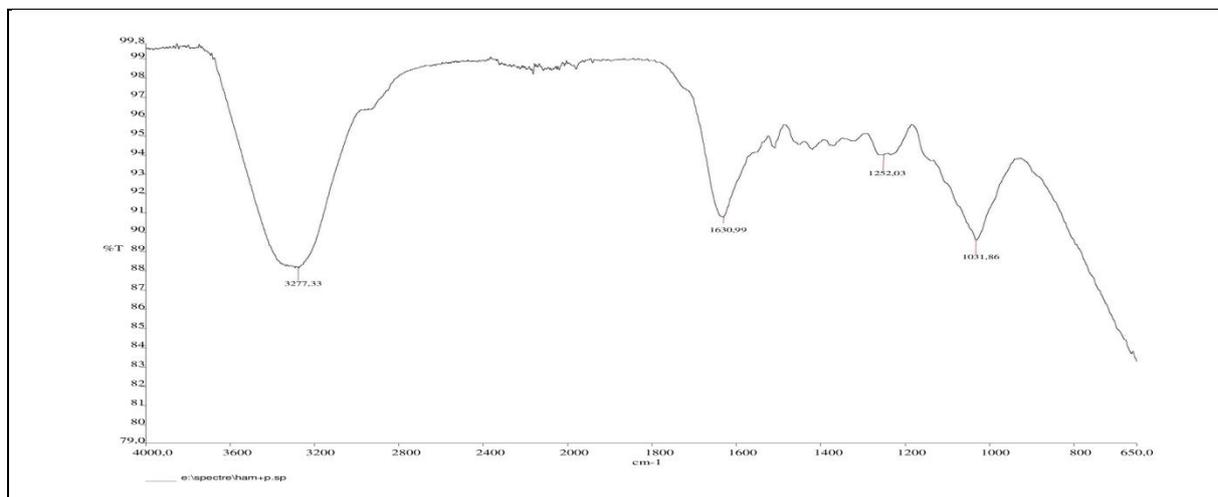


Figure 3b: FTIR Spectrum of groundnut shell after paracetamol sorption

The shifts in the absorption peaks generally observed indicate the existence of a paracetamol binding process taking place on the surface of groundnut shell.

3.2. Adsorption isotherms

The isotherm of adsorption is employed to establish the maximum capacity sorption of paracetamol onto groundnut shell. The resulting curves and two-isotherm parameters are compared to the experimental data at groundnut shell sorbent for paracetamol removal in Figure 4 and Table 4.

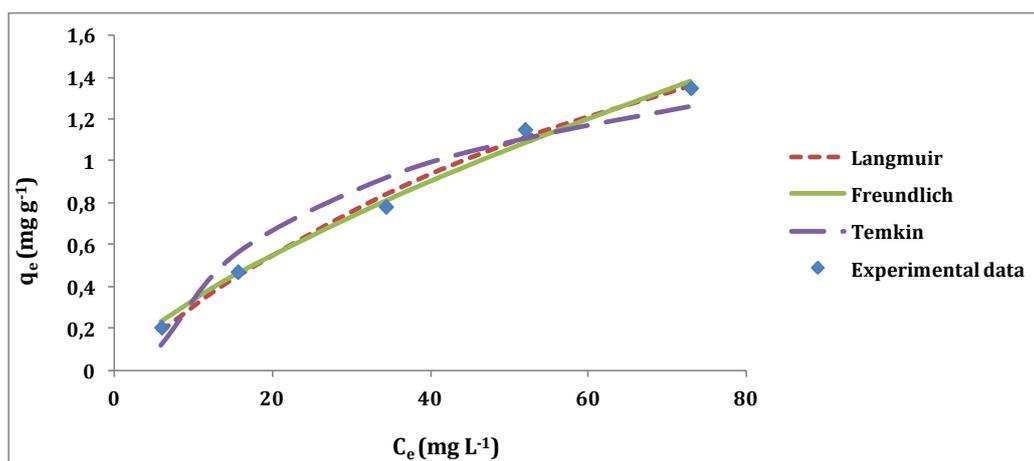


Figure 4: Comparison of measured and calculated q_e values for two-parameter isotherms

Table 4: Two- parameters isotherm models for paracetamol retention on the groundnut shell

Models	Parameters	Values
Langmuir	q_m	3.02
	K_L	0.011
	R_L	0.48
	SSE	0.0057
	R^2 (%)	99.62
Freundlich	$1/n$	0.71
	K_F	0.065
	SSE	0.0067
	R^2 (%)	99.55
Temkin	B_1	0.45
	K_T	0.22
	SSE	0.044
	R^2 (%)	97.09

The results compiled in Table 4 indicate that the Langmuir model fitted very well to the experimental data, showing high correlation coefficient R^2 value and the low SSE value compared to Freundlich and Temkin isotherms. This model estimated that the monolayer sorption capacity for paracetamol- groundnut shell system was of 3.02 mg.g^{-1} . The values of R_L , K_L and $1/n$ are in between zero and one give an indication of the favorability of the sorption of paracetamol onto groundnut shell sorbent. 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 paracetamol and groundnut shell sorbent. The abilities of the three-parameter equations, Sips, Redlich– Peterson and Toth, to model the equilibrium adsorption data were examined. The resulting curves and three-isotherm parameters are compared to the experimental data at groundnut shell sorbent for paracetamol removal in Figure 5 and Table 5.

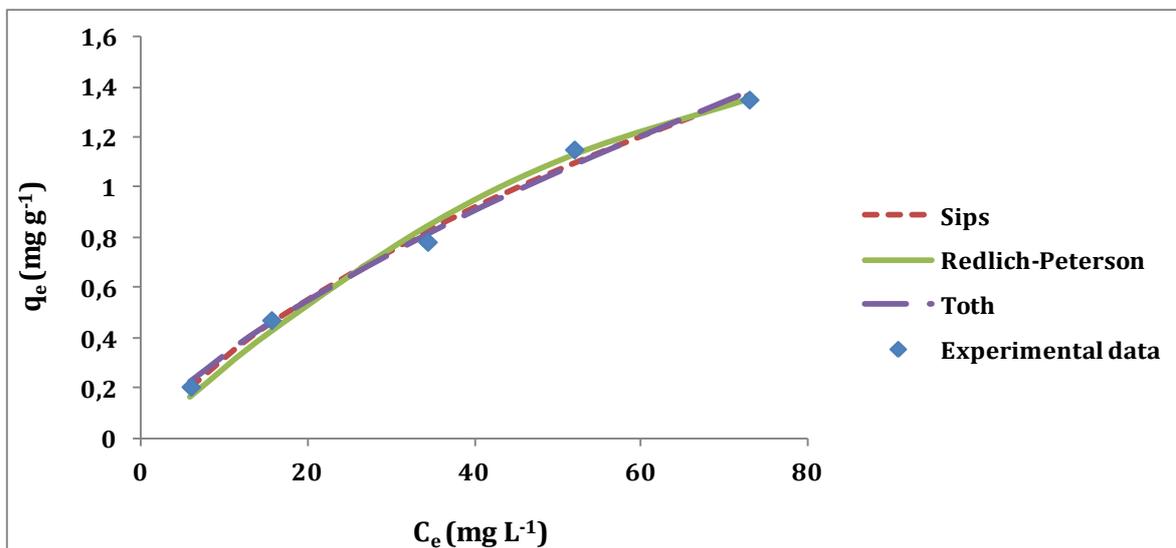


Figure 5: Comparison of measured and calculated q_e values for three-parameter isotherms

Table 5: Three- parameter isotherm models for paracetamol retention on the groundnut shell

Models	Parameters	Values
Sips	q_m	0.71
	K_S	0.088
	n	1.14
	SSE	0.0053
	R^2 (%)	99.65
Redlich-Peterson	K_{RP}	0.028
	α_{RP}	0.0005
	n	1.61
	SSE	0.0078
	R^2 (%)	99.48
Toth	q_m	1.81
	α_T	0.31
	n	0.079
	SSE	0.0063
	R^2 (%)	99.58

According to Table 5, the high correlation coefficient R^2 value and low SSE value for Sips isotherm suggests that it is the best curve model of experimental data for the sorption of paracetamol onto groundnut shell. The results obtained using the three-parameter equations show that the best-fitted sorption isotherm models were determined to be in the order: Sips > Toth > Redlich–Peterson. The maximum adsorption capacities predicted by the Sips and Toth isotherms were lower than the Langmuir isotherm. The values of Sips model exponent n (1.14) and the value of Redlich–Peterson model exponent n (1.61) indicated that the sorption data were more of Langmuir form. It can be concluded that the surface of groundnut shell is homogenous for paracetamol sorption.

Best adsorption capacity obtained for groundnut shell corresponding to 3.02 mg.g^{-1} (Table 4). This value is very low compared to the sorption capacity reached by [18] who reported a capacity removal of 515.27 mg.g^{-1} of commercial powdered activated carbon (PAC). It's clear that the capacity of groundnut shell for paracetamol in the experimental conditions used in this work is very low compared to the capacity shown by activated carbons but it must be taken into account that biosorbents efficiency is generally low relative to synthetic adsorbents. Conversely, the biosorbents have the advantage of no need of costly pretreatments.

On the other hand, the retention of paracetamol on the groundnut shell showed a relatively significant adsorption with a maximal quantity of 3.02 mg.g^{-1} (Table 4). This value is slightly higher than those reported in the literature using other raw sorbents such as *Posidonia Oceanica* (1.638 mg.g^{-1}) [18], grape stalk (1.74 mg.g^{-1}), yohimbe bark (0.77 mg.g^{-1}) and cork bark (0.99 mg.g^{-1}) [38], Sugar Can Bagasse (0.12 mg.g^{-1}) and Vegetable Sponge (0.037 mg.g^{-1}) [39]. From these results, we found that the retention of paracetamol by biomaterials is very low compared to conventional adsorbents. This could be due to the high hydrophilicity of paracetamol ($\log k_{ow} = 0.46$) [18; 40]. This study confirms that the paracetamol does not adsorb easily on the biomaterials. We can say that for to improve the retention capacity of paracetamol from water, the setting up of activation processes of the groundnut shell is necessary.

Conclusions

The goal of this study was to investigate the sorption capacity of paracetamol onto groundnut shell with using different two and three-parameter models. From the results obtained, the following comments can be made:

-Among two-parameter models, the Langmuir better described the isotherm data with high correlation coefficient R^2 and low value of SSE with maximum sorption capacity obtained for the groundnut shell is 3.02 mg.g^{-1} . The values of R_L , K_L and $1/n$ are in between zero and one. This confirms that the adsorption of paracetamol onto groundnut shell is favorable.

-In the case of three-parameter models, the Sips model was found to provide closest fit to the equilibrium experimental data.

This investigation indicates that groundnut shell could be considered as potential low cost sorbent for paracetamol removal from aqueous solution.

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