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Optimum sorption isotherm by linear and non-linear methods for Aspirin onto *Typha australis* leaves powder

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Abstract

Typha australis leaves were used as a low-cost sorbent for the removal of aspirin from aqueous solution in batch adsorption procedure. In order to estimate the equilibrium parameters, the equilibrium adsorption data were analyzed using the following two-parameter isotherms: Freundlich and Langmuir. A comparison of linear and non-linear regression methods in selecting the optimum adsorption isotherm was applied on the experimental data. Five linearized isotherm models (including four linearized Langmuir models) and two non-linear isotherm models are thus discussed in this study. The Sum of the Squares of the Errors (SSE), Chi-square (χ^2) and the correlation coefficient (R^2) between the calculated data and the experimental data by non-linear method were used. It was concluded that the nonlinear method is a better way to obtain the isotherm parameters and the data were in good agreement with the Langmuir isotherm model. *Typha australis* leaves powder can be considered as a new useful low cost natural biosorbent for pharmaceutical product clean-up operations in aquatic system.

1. Introduction

Pharmaceutical compounds have recently been recognized as emerging pollutant as they have been detected in almost all compartment of the environment especially in the water system [1; 2]. The presence of pharmaceuticals in water is attributable to personal hygiene products, pharmaceutical industry waste, hospital waste and therapeutic drugs. This is very alarming considering that pharmaceutical compounds are known to cause adverse effect to the environment even at low concentrations [3-5].

Aspirin or Acetylsalicylic acid is one of the most consumed and produced pharmaceutical compound. As a result, aspirin is also one of the most commonly detected pharmaceutical compounds in the environment. A lot of research is being done in order to find effective way to remove this type of compound. Advance treatments such as degradation [6], electrochemical

degradation [7] biodegradation [8], photocatalytic degradation [9] and adsorption [10] have shown positive results in removing this type of pharmaceutical compound.

Solid-phase adsorption is one of the most efficient technologies for the treatment of pharmaceutical compounds polluted water. The adsorption of pharmaceutical compounds onto activated carbon has attracted many researchers, but its high cost inhibits its application on a large scale [11; 12].

In order to overcome this problem, utilization of cheaper and indigenous waste material for the removal of pharmaceutical compounds from aqueous solutions has become a focal point of much study [13-17]. The focus of this research is to explore the possibility of using the *Typha australis*, an abundant and available plant along the Senegal River. In the present study both linear and non-linear methods were used to estimate the isotherm parameters of aspirin onto *Typha australis* leaves powder.

2. Experimantal details

2.1 Adsorbate

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

2.2 Adsorbent

Typha australis leaves were collected from the south of Mauritania (figure 1). According to N'diaye *et al.,* (2017) [18], the *Typha australis* leaves were washed thoroughly with ultra-pure water to remove dirt. The biomass was then air dried for 10 days followed by drying in an oven at 70 °C for 24 h. The dried biomass was ground, sieved to obtain particle sizes below 100 µm and stored in a dessicator before use. The physicochemical characteristics of the *Typha australis* leaves powder are given in Table 1 [18].

Figure 1: *Typha australis* along the Senegal River

Table 1: Physicochemical characteristics of *Typha australis* leaves powder

Parameters	Mean
pHpzc	6.36
Moisture (%)	3.9
Ash (%)	9.9
Loss of mass ignition (%)	16.9
Total surface acidity (meq g^{-1})	0.744
Total surface basicity (meq g^{-1})	0.376
Surface area (m^2 g^{-1})	0.91
Particle size (µm)	<100

2.3 Adsorption experiments

The sorption isotherms at ambient temperature are obtained by mixing (70 rpm), for 180 minutes, 0.5 g of *Typha Australis* leaves powder with 50 mL of aspirin solutions with different concentrations (0-100 mg L^{-1}). At the end of each experiment the 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} [19] at a selected wave length of 222 nm. 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 *Typha australis* leaves powder (mg g^{-1}),
- C_i: initial solution concentration of aspirin (mg L^{-1}),
- C_e: equilibrium solution concentration of aspirin (mg L^{-1}),
- m: *Typha australis* leaves powder weight (g),

The data were fitted to Langmuir and Freundlich isotherms to find the best fitted isotherm. The linear and non-linear mathematical expressions of Langmuir and Freundlich models are summarized in Table 2.

Table 2: Isotherms and their Linear and Nonlinear Forms

Model	Equation	Linear expression	Plot
Langmuir-1	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	$\frac{C_e}{q_e} = \frac{C_e}{q_e} + \frac{1}{K_L q_m}$	$\frac{C_e}{q_e}$ sv. C_e
Langmuir-2		$\frac{1}{q_e} = \left(\frac{1}{K_L q_m}\right)\frac{1}{C_e} + \frac{1}{q_m}$	$\frac{1}{q_e}$ sv. $\frac{1}{C_e}$
Langmuir-3		$q_e = q_m - \left(\frac{1}{K_L}\right)\frac{q_e}{C_e}$	q_e sv. $\frac{q_e}{C_e}$
Langmuir-4		$\frac{q_e}{C_e} = K_L - K_L q_e$	$\frac{q_e}{C_e}$ sv. q_e
Freundlich	$q_e = K_F C_e^{1/n}$	$\log q_e = \log K_F + \frac{1}{n}\log C_e$	$\log(q_e)$ sv. $\log(C_e)$

The Sum of the Squares of the Errors (SSE), Chi-square (χ^2) and the correlation coefficient (R^2**)** values are determined respectively by following equations (2), (3) and (4):

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

$$\chi^2 = \sum((q_{exp} - q_{mod})^2 / q_{mod}) \qquad (3)$$

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

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

Out of the four different type of linearized Langmuir isotherm equations, Langmuir-1 and Langmuir-2 are the most commonly used by several researchers because of the minimized deviations from the fitted equation resulting in the best error distribution [20; 21].
The q_m and K_L values of Langmuir-1, Langmuir-2, Langmuir-3 and Langmuir-4 were predicted from the plot between C_e/q_e versus C_e, $1/q_e$ versus $1/C_e$, q_e versus q_e/C_e and q_e/C_e versus q_e, respectively. Figures 2 to 5 show the four linear Langmuir equations with the experimental data for the sorption of aspirin onto *Typha australis* leaves powder. The calculated isotherm parameters are shown in Table 3.

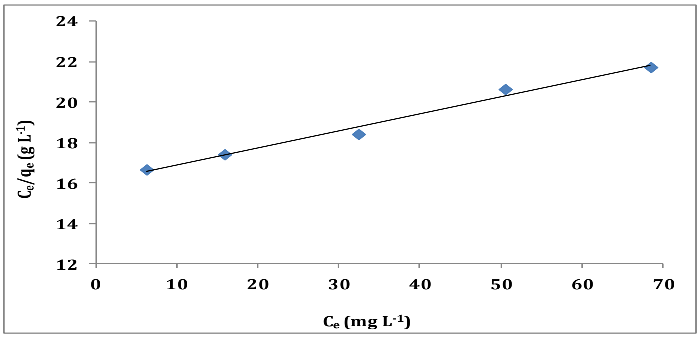

Figure 2: Langmuir-1 isotherm obtained using the linear method for the sorption of Aspirin onto *Typha australis* leaves powder

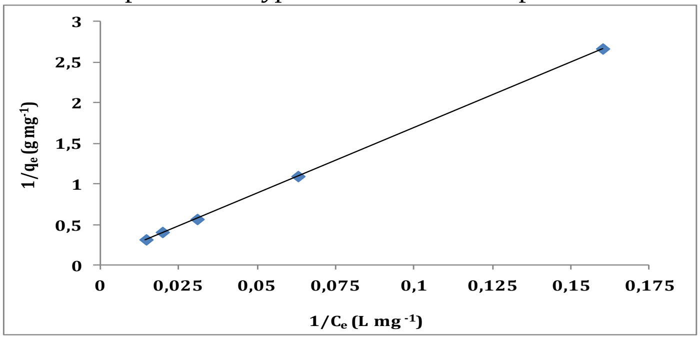

Figure 3: Langmuir-2 isotherm obtained using the linear method for the sorption of Aspirin onto *Typha australis* leaves powder

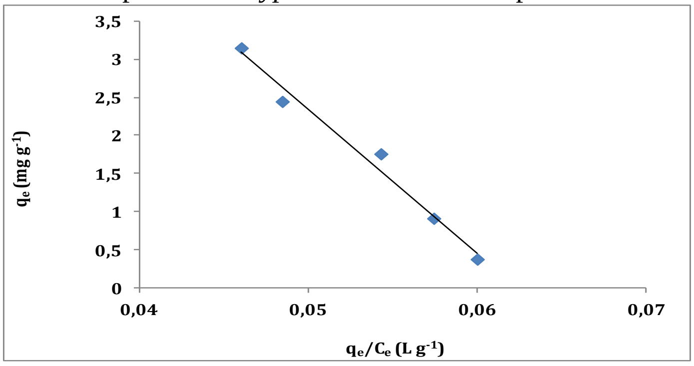

Figure 4: Langmuir-3 isotherm obtained using the linear method for the sorption of

Aspirin onto *Typha australis* leaves powder

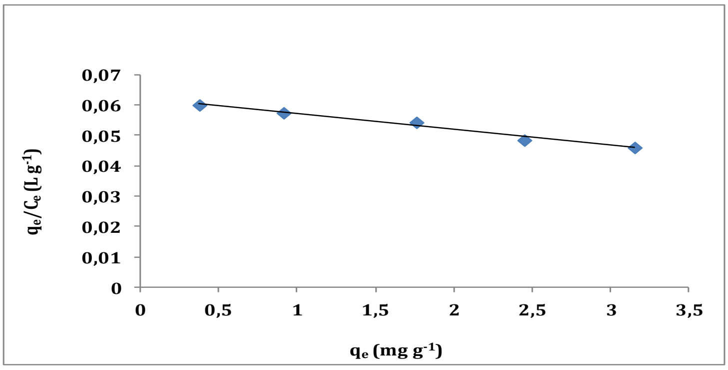

Figure 5: Langmuir-4 isotherm obtained using the linear method for the sorption of Aspirin onto *Typha australis* leaves powder

Table 3: Isotherm Parameters for aspirin sorption onto *Typha australis* leaves powder obtained by using the Linear Method

Models	Parameters	Mean
Langmuir-1	$\mathbf{q_m}$	11.86
	$\mathbf{K_L}$	0.0052
	^{2}R	0.986
Langmuir-2	$\mathbf{q_m}$	12.5
	$\mathbf{K_L}$	0.0049
	^{2}R	1
Langmuir-3	$\mathbf{q_m}$	11.76
	$\mathbf{K_L}$	0.0053
	^{2}R	0.981
Langmuir-4	$\mathbf{q_m}$	11.96
	$\mathbf{K_L}$	0.0052
	^{2}R	0.981
Freundlich	**1/n**	0.89
	$\mathbf{K_F}$	0.076
	^{2}R	0.998

From table 3, it was observed that the Langmuir constants varied for different forms of linear Langmuir equations. Further out of the R^2 for Langmuir-1, Langmuir-2, Langmuir-3 and Langmuir-4, R^2 value for Langmuir-2 was found to be relatively higher and followed by Langmuir-1. In addition, Langmuir-3 and Langmuir-4 showed a similar R^2 value confirming that both these types are in same error distribution structure.

From Table 3, it was also observed that the equilibrium sorption capacity of *Typha australis* leaves powder for aspirin was found to be 11.86 and 12.5 mg g^{-1} for Langmuir-1 and Langmuir-2, respectively. The very high sorption capacity of this material confirms that the *Typha australis* leaves powder can be used as an adsorbent for the removal of aspirin from aqueous solutions.

The equilibrium data were further analyzed using the linearized form of Freundlich equation using the same set of experimental data, by plotting log (q_e) versus log (C_e) (figure 6). The Freundlich constant K_F and Freundlich exponent 1/n were calculated from the intercept and slope of the plot, respectively. It is observed that the Freundlich constant K_F is 0.076 (mg g^{-1}) (Lmg^{-1}) ^{n} and exponent 1/n is 0.89.

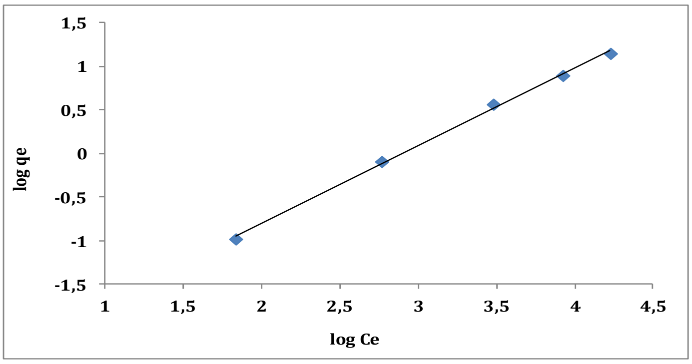

Figure 6: Freundlich isotherm obtained using the linear method for the sorption of Aspirin onto *Typha australis* leaves powder

The calculated Freundlich isotherm parameters and the corresponding R^2 value were shown in Table 3. From Table 3, the R^2 values were found to be relatively less than best fit linearized Langmuir-2 isotherm. This suggests that the Langmuir isotherm as the most appropriate isotherm than the Freundlich isotherm for the present system.

Non-linear method had an advantage that the error distribution does not get altered as in linear technique, as all the isotherm parameters are fixed in the same axis. For nonlinear method, a trial and error procedure, which is applicable to computer operation, was developed to determine the isotherm parameters by minimizing the respective R^2 between experimental data and isotherms using the solver Excel [20; 21]. The isotherm curves of aspirin adsorption onto *Typha australis* leaves powder sorbent are studied and represented in Figure 7, then modeled using the isotherm equations of Langmuir and Freundlich. Isotherm model parameters are given in Table 4.

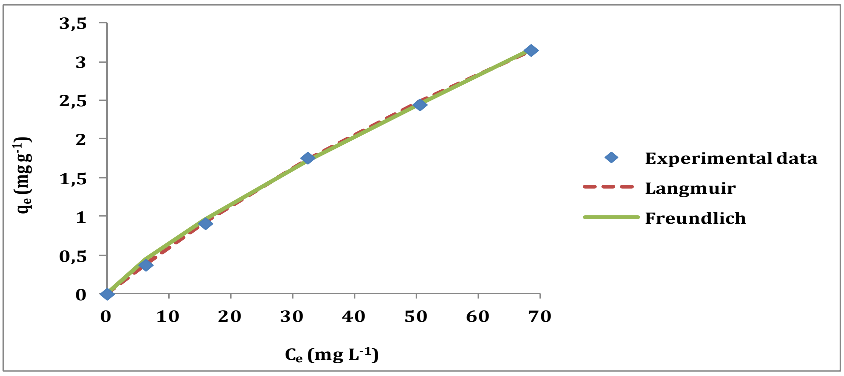

Figure 7: Langmuir and Freundlich non linear for *Typha australis* leaves powder

Table 4: Isotherm Parameters for aspirin sorption onto *Typha australis* leaves powder obtained by using the Nonlinear Method

Models	Parameters	Mean
Langmuir	q_m	11.74
	K_L	0.0053
	SSE	0.0029
	χ^2	0.0013
	^{2}R (%)	99.94
Freundlich	1/n	0.82
	K_F	0.098
	SSE	0.0086
	χ^2	0.0129
	^{2}R (%)	99.83

The values of R^2 are compared, Langmuir isotherm are shown to have higher value than Freundlich isotherms. The lowest SSE and χ^2 values further confirmed the suitability of Langmuir model in describing the equilibrium data, suggesting the existence of monolayer adsorption of aspirin onto *Typha Australis* leaves powder sorbent.
From Table 4, it is observed that the Langmuir isotherm constants determined by the nonlinear method are quite close to the results of Langmuir-1 (see table 3). In addition, it is observed that the Freundlich isotherm constants determine by the linear and nonlinear method are significantly different.
The analysis of equilibrium data shows that it is not sufficient to use the R^2 of the linear method for comparing the best-fitting isotherm. The non-linear curve fitting analysis method is found to be the more appropriate method to determine and confirm that the equilibrium data are best described by the Langmuir isotherm model.
Based on the Langmuir, the monolayer adsorption capacity of *Typha australis* leaves powder is found to be 11.74 mg g^{-1}. This result shows that the *Typha australis*, an abundant and available plant along the Senegal River can be used as an adsorbent for the removal of aspirin from aqueous solution. A list showing the adsorption capacity of different low-cost sorbents for the sorption of different pharmaceutical products from their aqueous solutions is given in Table 5. From Table 5, it is observed that the adsorption capacity of *Typha australis* leaves powder for aspirin uptake is higher or comparable with other low cost sorbents.

Table 5: Adsorption capacities of different Low-cost sorbents for the uptake of different pharmaceutical products from their aqueous solutions

Adsorbent	Adsorbate	Adsorption capacity (mg g^{-1})	Reference
Kaolinite	Triclosan	7.73	[22]
grape stalk	Paracetamol	1.74	[23]
yohimbe bark	Paracetamol	0.77	
cork bark	Paracetamol	0.99	
pine wood biochar	ibuprofen	10.74	[24]
Narural clay	ibuprofen	3.52	[25]
	naproxen	2.78	
	carbamazepine	3.40	
Posidonia Oceanica	Paracetamol	1.638	[26]
Dehydrated sewage sludge	Paracetamol	0.956	
groundnut shells	Paracetamol	3.02	[27]
Balanites aegyptiaca seeds	Caffeine	4.28	[28]
Typha australis leaves	Aspirin	11.74	Present study

The capacity of aspirin onto *Typha australis* leaves powder was lower value than that obtained by Wong et al, (2017) [29], for aspirin adsorption with 178.57 mg g^{-1} of activated carbon from spent tea leaves. Likewise, the capacity of aspirin onto *Typha australis* leaves powder was lower values than that obtained by Ferreira et al. (2015) [30], for paracetamol adsorption with 64.75 mg g^{-1} and 58.91 mg g^{-1} onto activated carbons of dende and babassu coconut mesocarp, respectively.
In addition, when comparing the sorption capacity for the same specific surface area, the amount of aspirin adsorbed per square meter of *Typha australis* leaves powder (12.90 mg m^{-2}) is higher than that obtained by Hoppen et al, (2018) [31] with a activated carbon of babassu coconu mesocarp (0.12 mg m^{-2}) and that obtained by Wong et al, (2017) [29] with activated carbon derived from spent tea leaves (0.15 mg m^{-2}).

Although aspirin is less hydrophilic (log k_{ow} = 1.18) than most pharmaceuticals and the medium play an important role the retention of pharmaceuticals from aqueous solution. However, further studies are needed to develop activated from the *Typha australis* leaves powder.

Conclusion

Present study shows that the non-linear method is the better way to obtain the adsorption parameters than the linear method. Langmuir isotherm well represents the sorption of aspirin onto *Typha australis* leaves powder. Non-linear is the more appropriate method to obtain the isotherm parameters. These results indicated that *Typha australis* leaves powder can be successfully used for the removal of aspirin from aqueous solutions.

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