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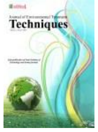

# Sorption of Aspirin from Aqueous Solutions using Rice Husk as Low Cost Sorbent

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## Abstract

The Rice Husk (RH) was used as low cost sorbent for the removal of aspirin by sorption from aqueous solution. The RH was characterized by using the point of zero charge (pHpzc), Boehm titration and Fourier transform infrared spectroscopy (FTIR). Batch sorption experiments are intended to identify the adsorption isotherms of aspirin on the RH. The experimental data were fitted to the Langmuir and Freundlich isotherms. The Sum of the Squares of the Errors (SSE) and the correlation coefficient $R^2$ between the calculated and the experimental data by nonlinear regressive analysis were used. The Langmuir model better described the isotherm data with the maximum Langmuir monolayer adsorption capacity was 47.03 mg $g^{-1}$ at pH 2. As a conclusion, RH could be one of the low cost and environmentally friendly sorbent.

**Keywords**: Aspirin, Rice Husk, low cost sorbent, isotherms

## 1 Introduction

Aspirin or Acetylsalicylic acid is a non-steroidal anti-inflammatory drug used to treat pain, fever and inflammation [1] and prevention of first myocardial infarction, cardiovascular diseases, cancer and treatment of human immuno-deficiency virus infection [2].As a result, aspirin is also one of the most commonly detected pharmaceutical compounds in the environment [3-5].

Several methods to treat pharmaceutical pollutants have been reported, such as via electrochemical advanced oxidation processes [6], photocatalysis [7], membrane filtration [8] and adsorption process [9; 10]. However the adsorption is seen as the most promising removal method because of its versatility in removing different pollutant and also its efficiency. In adsorption processes the cost of commercial activated carbons may be limiting, creating necessity to develop new materials with lower investment.

An alternative is the utilization of agricultural residues directly as sorbents or as precursors to activated carbon synthesis, since these materials are inexpensive, or even free, available in large quantities and renewable [11]. Low-cost sorbents including raw agricultural solid wastes and waste materials from forest industries have been used successfully as alternative to high cost commercial activated carbon [12].

Therefore, in this study, a local agricultural, cheap, ecofriendly, abundant and solid waste material Rice Husk (RH) selected for the removal of aspirin from aqueous solution. The point of zero charge (pHpzc), Boehm titration, Fourier and transform infrared spectroscopy (FTIR) analyses were performed. The equilibrium data were described by the Langmuir and Freundlich isotherm models with using the nonlinear method.

## 2 Material and methods

### *2.1 Aspirin solutions*

All the solutions are prepared using pure 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. The physico-chemical properties of aspirin are given in table 1.

Table 1: Physico- chemical properties of aspirin

| **Chemical name** | Acetylsalicylic Acid |
|---|---|
| **Molecular formula** | $C_9H_80_4$ |
| **Molecular weight (g mol$^{-1}$)** | 180.16 |
| **Water solubility (g L$^{-1}$)** | 3.3 (20 ℃) |
| **pKa** | 3.5 (25 ℃) |
| **Log K$_{ow}$** | 1.18 |

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### *2.2 Preparation and characterization of RH*

The agricultural wastes, RH, are collected from the south of Mauritania. RH was crushed, sieved, thoroughly rinsed with distilled water and then dried at 105 °C for 2 h until reaching a constant weight. Finally, the RH was powdered, sieved (< 100 µm) and stored in desiccator before use (figure 1).

Figure 1: RH before and after grounding

The point of zero charge (pHpzc) of the RH was carried out [13] and the surface area was obtained using Sears method [14]. The surface acidic and basic functional groups of the RH were determined by the acid-base titration method proposed by Boehm [15]. The samples of RH were analyzed by the Fourier transform infrared spectroscopy (FTIR) to determine the surface functional groups. The wavenumber scanning is in the range of 650–4,000 cm$^{-1}$.

### *2.3 Adsorption isotherms*

The sorption isotherms at ambient temperature (25 °C) are obtained by mixing (70 rpm), for 180 minutes, 0.5 g of sorbent with 50 mL of aspirin solutions with different concentrations varying from 10 to 100 mg L$^{-1}$. The pH of the solutions was adjusted using a pH-meter to constant values by drop-wise addition of 0.1 M HCl or 0.1 M NaOH solutions. 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$^{-1}$ [16] at a selected wave length of 222 nm.

The adsorbed quantity at equilibrium ($q_e$) is calculated according to the following equation (1):

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

where:

- $q_e$: quantity of aspirin per g of RH (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 RH weight (g),
- V: Volume of the solution (L).

Adsorption isotherm gives an idea about the feasibility of a sorbate–sorbent system. In this work Langmuir and Freundlich models were tested for describing the experimental results. The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The Freundlich model is commonly used to describe the adsorption characteristics for a heterogeneous surface [17]. The Langmuir and Freundlich models can be expressed as (2) and (3), respectively:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{2}$$

$$q_e = K_F C_e^{1/n} \tag{3}$$

where $q_m$ and $k_L$ are Langmuir constants related to adsorption capacity and affinity of the binding sites, respectively. $k_F$ and n are Freundlich constants representing adsorption capacity and the energy of adsorption effectiveness, respectively.

The factor of separation of Langmuir, $R_L$, which is an essential factor characteristic of this isotherm is calculated by using the relation (4):

$$R_L = \frac{1}{(1 + k_L C_0)} \tag{4}$$

where $C_0$ is the higher initial concentration of aspirin, while and $q_m$ is the Langmuir constant and the maximum adsorption capacity respectively. The parameters indicate the shape of the isotherm as follows: $R_L$ values indicate the type of isotherm. When $R_L = 1$ adsorption is linear; when $0 < R_L < 1$, it is favourable, when $R_L = 0$, it is irreversible, while to be unfavorable, while when $R_L > 1$, it is unfavorable.

The correlation coefficient R$^2$ and the Sum of the Squares of the Errors (SSE) analysis is used to fit experimental data with isotherm using the Excel Solver determined by following equations (5) and (6), respectively:

$$R^2 = 100\left(1 - \frac{\left\| q_{exp} - q_{mod} \right\|^2}{\left\| q_{exp} - q_{avr} \right\|^2}\right) \tag{5}$$

$$\mathrm{SSE} = \left(q_{\exp} - q_{\mathrm{mod}}\right)^2 \tag{6}$$

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 discussion

### *3.1 Characterization of RH*

The physical and chemical characteristics of RH sorbent are described in table 2. The quantification of the RH sorbent by Boehm titration reveals that the sorbent has also the greatest content of acidic surface than the basic surface groups. The predominance of acidic surface is confirmed by pH$_{pzc}$ value of 5.8. The retention area for RH, without any thermal and /or chemical process, is found to be 5.6 $m^2$ $g^{-1}$. To determine the surface functional groups of RH, its FTIR spectrum is obtained as shown in Figure 2. O–H stretching of the hydroxyl of the alcohols groups and bonded hydroxyl groups of cellulose: 2925 $cm^{-1}$.

Table 2: Physical characteristics of the RH

| **Parameters** | **Value** |
|---|---|
| **$pH_{pzc}$** | 5.8 |
| **Total surface acidity (**meq $g^{-1}$**)** | 0.600 |
| **Total surface basicity (**meq $g^{-1}$**)** | 0.155 |
| **Specific surface** ($m^2$ $g^{-1}$) | 5.6 |
| **Particle size** (µm) | < 100 |

The peak at 2854.3 $cm^{-1}$ was assigned to C–H asymmetrical stretching of methyl groups on the surface of RH adsorbent. Peak at 1743.9 $cm^{-1}$ (C =O stretching of COOH). The peak lying in the region of 1036.6 $cm^{-1}$ 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 sorption sites for aspirin removal.

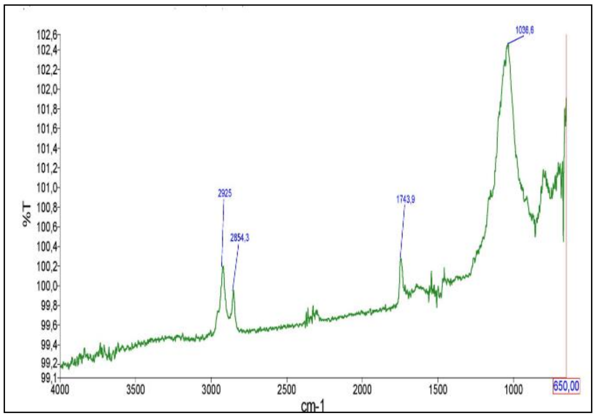

Figure 2: FTIR Spectrum of RH

### *3.2 Adsorption isotherms*

The adsorption isotherm gives an idea of the equilibrium behavior of an aspirin–RH system. Figures 3, 4 and 5 shows the experimental equilibrium data and the predicted theorical isotherms for the sorption of aspirin onto RH at pH 2, 7 and 12, respectively. The values of isotherm parameters that are studied in this work are shown in Table 3.

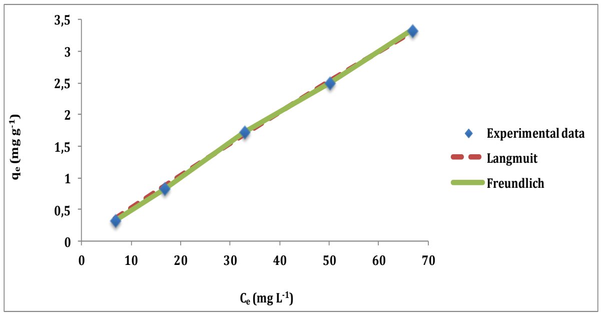

Figure 3: Langmuir and Freundlich non linear for RH at pH 2

The values of $R^2$ are compared, Langmuir isotherm are shown to have slightly higher than Freundlich isotherm. The lowest SSE value further confirmed the suitability of Langmuir model in describing the equilibrium data, suggesting the existence of monolayer adsorption of aspirin onto RH. Furthmore, it can be seen from table 3 that all values of $K_L$, $R_L$ and 1/n are in between zero and one. This confirms that the adsorption of aspirin onto RH. 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 RH sorbent.

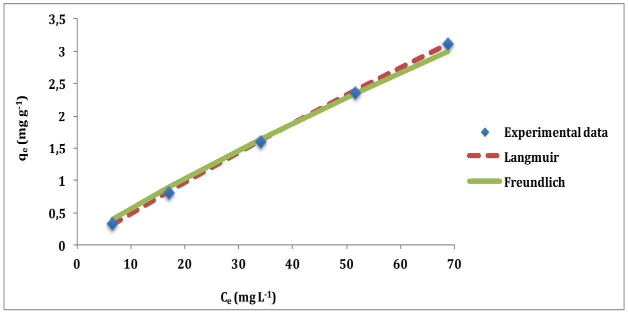

Figure 4: Langmuir and Freundlich non linear for RH at pH 7

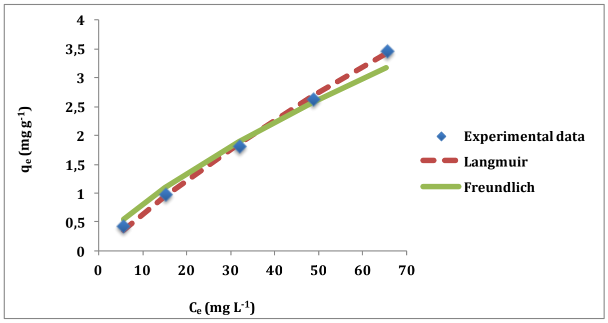

Figure 5: Langmuir and Freundlich non linear for RH at pH 12

Table 3: Isotherm parameters with nonlinear methods

| Models | pH | 2 | 7 | 12 |
|---|---|---|---|---|
| **Langmuir** | $q_m$ | 47.03 | 33.36 | 17.30 |
| | $K_L$ | 0.0011 | 0.0015 | 0.0038 |
| | $R_L$ | 0.90 | 0.87 | 0.72 |
| | SSE | 0.0055 | 0.0018 | 0.0119 |
| | $R^2$ (%) | 99.51 | 99.97 | 99.81 |
| **Freundlich** | 1/n | 0.81 | 0.87 | 0.72 |
| | $K_F$ | 0.108 | 0.077 | 0.154 |
| | SSE | 0.104 | 0.0242 | 0.1189 |
| | $R^2$ (%) | 98.24 | 99.52 | 98.01 |

The best pH for the adsorption of aspirin is pH 2 which is the initial pH of aspirin without addition of NaOH. A decrease in adsorption was observed with an increase in pH. The adsorption capacity decrease from 47.03 mg $g^{-1}$ at pH 2, to 33.36 and 17.30 mg $g^{-1}$ at pH 7 and 12. The same finding was reported from previous study where the adsorption of aspirin favours a more acidic solution [9; 10].

The $pH_{PZC}$ is an important parameter for biosorbent to characterize the sensitivity to the pH and their surface charges. The pHpzc value is a key factor in the electrostatic interactions between sorbate and sorbent. The $pH_{PZC}$ of RH was found to be 5.8. This means that at pH more than 5.8, the RH sorbent surface will be negatively charged. Aspirin is a weak acid (pKa = 3.5) and undergoes partial deprotonation in water to produce negatively charge ions (figure 6). By increasing the pH of aspirin solution, the surface of RH and aspirin will be negatively charged resulting in electrostatic repulsion which hindered the adsorption [1; 18].

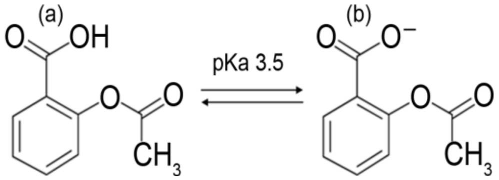

Figure 6: Protonated (a) and unprotonated (b) aspirin structure [19]

Moreover, the interactions between sorbate-sorbent are strongly influenced by medium pH. Which explain RH adsorption drop from 47.03 $mg\ g^{-1}$ at pH 2 to 17.30 $mg\ g^{-1}$ at pH 12. The same finding was reported by Moreno-Castilla (2004) [20]. Best adsorption capacity obtained for RH occurred at pH 2 corresponding to 47.03 $mg\ g^{-1}$.This value is inferior than that reported by Hoppen et al. (2018) [21] for aspirin onto activated carbon of babassu coconut mesocarp with 72.441 $mg\ g^{-1}$ at pH 2. Value attained for RH is lower than that obtained by Ferreira et al. (2015) [22] for paracetamol adsorption with 64.75 $mg\ g^{-1}$ and 58.91 $mg\ g^{-1}$ at pH 2 onto activated carbons of dende and babassu coconut mesocarp, respectively. Similarly, the capacity of aspirin adsorption onto RH is lower than that obtained by Portinho et al. (2017) [23] for caffeine adsorption with 68.633 $mg\ g^{-1}$ at pH 2 onto Grape Stalk. Like other pharmaceuticals, for to improve the retention capacity of aspirin, the setting up of activation processes (thermal and / or chemical) of the RH is necessary.

## 4 Conclusions

The aim of this study was to investigate the adsorption capacity of aspirin onto RH. The RH was characterized by using pHpzc, Boehm titration and FTIR. The isotherm data of aspirin retention give a good fit with Langmuir model and shows a monolayer adsorption. The maximum adsorption capacity obtained for the RH is 47.03 $mg\ g^{-1}$ at pH 2. The present study showed that the powdered RH is a promising sorbent for the removal of aspirin from aqueous solution, since the raw material RH was easily available in large quantity and the treatment method of biomaterial seemed to be economical.

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