Role of Rice Husk as Natural Sorbent in Paracetamol Sorption Equilibrium and Kinetics

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Abstract: Biosorbent of rice husk was utilized to evaluate the removing of paracetamol from aqueous medium by sorption process (batch-concept); studying the influence of several experimental parameters as biosorbent dose, contact time, change of temperature; also studying the behaviour of the equilibrium isotherm of paracetamol into the rice husks and comparing the data with different isotherm models. Pseudo-second order equation and Langmuir model were best suited for data experience. With increasing temperature the sorption process increased; suggesting that the process is endothermic in nature. FTIR test was tested before and after sorption for the purpose of showing the presence and number of the functional groups of paracetamol binding on to the tested sorbent.

Keywords: Biosorbent; rice husk; paracetamol; batch; temperature; FTIR.

1. Introduction

Paracetamol, or 4-hydroxyacetanilide, is a multi-use drug for the purpose of reducing headaches and to prevent or reduce fever [1, 2, and 3]. Its availability by prescription and it is given as an over-the-counter-medicine. A public health problem is accessibility to pain medication due to a lot of exhaustion of drugs, as paracetamol, by people. Nevertheless, there are a lot of pharmaceutical products; there are amounts of drug taken that cannot be absorbed by the body, thus, released to environment by display from the system of the sewage. Commonly, expired or unused Paracetamol is disposed of, so causes environmental problems when entering groundwater equipment. Lots of medicines are non-biodegradable; the deposit may exist in treated-water and in drinking water [2, 4]. The fundamental physicochemical characteristics and composition of paracetamol are shown in Table 1. [1]:

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Table 1. Physical-chemical paracetamol specifications.

| Drug      | Molecular Weight (g/mol) | Log P  | SoH₂O(25°C)(mg/l) | pKa |
|-----------|--------------------------|--------|------------------|-----|
| Paracetamol | 151.2                   | 0.46   | 14               | 9.38|

*spheres in black denote to atoms of carbon, while in red denote to atoms of oxygen, spheres in blue denote to nitrogen atoms and the white color denote to hydrogen atoms.

The same specifications in Table 1 simplify paracetamol accumulation in soil and its presence in water [1, 5, and 6]. As the product of pharmaceutical is non-biodegradable; and has a bad effect not only on the environment but on the human health and life of other organisms [2]. The traditional approach of sewage treatment which uses physical, chemical and biological concepts failed in limit or reduces the plurality of these components and they are partly eliminated; so dismissal remains collects in drinking water equipment [2]. However, these micro-pollutants revelations have been upgraded in the last few years [4]. Most of these micro-pollutants exposed are in low concentration; ranges between a gram to nanogram/liter. And so on, these residues remain and with the passage of time; it will slowly accumulate and cause unwitting effect in the long-term [7]. Developed technologies such as: reverse-osmosis; ozonation, and membrane-filtration may ensure the sorption and removing of paracetamol and pharmaceuticals from drinking water. Because acetaminophen is an organic compound; the process of ozonation is active in eliminating it by immersing water in ozone to simplify organic breakdown. Membrane-filtration and Reverse-osmosis may efficiently isolate water from paracetamol as the membrane is selectively preventing it from water entry to the other side due to its size [2, 8]. The main disadvantages of this process are that it is much cost and to set it up in each wastewater treatment plant soon impossible.

Sorption on porous solids is a typical concept in order to eliminate organic and inorganic contaminants [1, 9]. Activated carbon is one of the most utilized sorbents due to its fluctuation and appropriate characteristics, like a high surface area, porosity and qualitative chemical characteristics that permit reacting with various chemical compounds. Actually, the capacity of sorption by activated carbon highly builds on the specified reactions between sorbent and sorbate; which conversely majorly depend upon their chemical characteristics [9].

In the search, many solute characteristics that affect organic solute sorption by activated carbon were searched. Some researchers have attempted immediately with respect to coefficient of octanol–water (K<sub>ow</sub>) to the capacity of sorption [10, 11]. A perfect relevance between this characteristic and sorption was most select for the hydrophobic contaminants onto activated carbons. Generally; a slight relation appeared whenever the solutes were little and hydrophilic [10, 12]; or for aromatic compounds [10, 13]. When compounds are aromatic many researchers have suggested that these compounds are possible adsorbed on activated carbons by dispersal interactions between π – electrons of the aromatic ring and the layers of graphene [10, 14].

Function of those sorbent or the sorbate influence profound effects on these dispersion reactions [10]. The examination of sorption of paracetamol by activated carbon is appropriate because this compound is a protrude contaminant; therefore, the traditional water treatment methods ineffective for removal. Adsorption is a multilateral mechanism, appropriate for more discoveries. The
sorption of pharmaceutical compounds from an aqueous solution by activated carbon was basically because of reactions between the functional groups of structure of drug and the groups on the surface of solid sorbent [1, 15]; addition, the basic property of activated carbon is the high-micro-porosity, exceeding its surface area for sorption and chemical interactions. Adding to that; and because of this features, is utilized in filtration and refinement process [2]. Due to the high cost of activated carbon, it is widely used as adsorbent. For this, Many researchers have been carried out for using the low-cost adsorbent that is resulted from various wastes and by-products such as rice-husk-as, coconut-husk, Neem-bark, pellets of peanut-hull, tea-wastes, sugarcane-Bagasse, cow-bone charcoal, tamarind fruit-shell, sawdust, etc[16, 17]. This search shows the possibility of using the rice-husk as a low-cost sorbent.

2. Materials and methods:

2.1 Prepare the Solution of Paracetamol (PC) and sorbent:

A PC solution has been prepared by dissolution of a known weight of PC in distilled water. To adjust pH of solution to desired value using 0.1M (HCl) acid or (NaOH)solutions; while, Rice husk(sorbent) is prepared by grinding and sieving to obtain a grain girth of range less than 0.6mm in diameter, and washed by distilled water, and dried by oven at 105°C for 24hr and stored in a dryer until use.

2.2 Procedure of Sorption

At room temperature (25±2°C) and pH7; tests of the batch were tested on a rotary shaker (SI-600R Lab. Companion) at 200rpm with 40ppm of PC concentration, utilizing glass tapered tubes. In all trials a specific-mass of sorbent used was mixed and shaken at a constant speed insolution of PC. At the end of shaking, the sorbent was removed from the solution by filtration using Filter paper (Whatman70mm). The remaining PC concentration was found when calculating the variation between the initial (C_i) and final (C_f) concentration of PC. Calculate the certain-sorbent uptake q (mg) of dry-solid using equation below [18]:

\[ q = (C_i - C_f) \times \frac{V}{w} \]  \hspace{1cm} (1)

Where: V in Liter which denotes to solution volume; and w(g) is a quantity of dry sorbent utilized.

3. Results and Discussion:

3.1 Effect of Rice-Husk Amount:

At pH7 and 200rpm with 1hr contact time; the amount of rice husk varying from 1gm until 5.5gm in order to find the best amount that gives a high removal of PC. Fig.1 shows the result below:
From this result; the optimum amount was at 4.5gm, with removal efficiency of about 78.63%; in case of increase removal ratio of PC with increase in sorbent amount explainable as increase in sorbent amount, lots of surface areas are available for PC to adsorb and thus causes increase in the sorption rate [17, 19]. And by increasing the amount of rice husk, there were no many changes in the removal ratio (adsorption capacity was steady); due to an effect of screen between sorbent, this cause a block of the sorbent effective sites with increase of sorbent in the system [20, 21].

3.2 Effect of Contact Time:
According to the result achieved from the experiments showing the influence of contact time on the process of sorption which appears below (Fig. 2); the rate of removal ratio of PC was increasing with increased time from 15 to 120min (rice husk amount was 4.5gm). Maximum removal was occurred at 90min (equilibrium). It can be dissected by that at first for sorption large number of vacant locations was obtainable; which retard subsequent because of exhaustion of the residual surface s and force of repulsive between the solute molecule and bulk phase [22, 17].

3.3 The effect of temperature:
Studying the effect of various temperatures (25, 30, 25, 35, 40 and 45°C) and the thermodynamic parameters such as \((\Delta H^o)\), \((\Delta S^o)\), \((\Delta G^o)\) are necessary to estimate whether the reaction of adsorption is endothermic or exothermic. The thermodynamic parameters were calculated from Eqs. (2) and (3) [22]:

\[
\ln K_d = \left(\frac{\Delta S^o}{R}\right) - \left(\frac{\Delta H^o}{RT}\right) \tag{2}
\]

\[
\Delta G^o = \Delta H^o - \Delta S^o T \tag{3}
\]

Where \(K_d\) is the coefficient of distribution; \((\Delta H^o)\), \((\Delta S^o)\), and the enthalpy \(T\); entropy, and temperature in Kelvin, sequentially; \(R\) is the constant of gas(8.314J/molK) and \(\Delta G^o\) is Gibbs free energy change. A result of changing temperature; values of distribution coefficient and thermodynamic parameters are presented in Fig.3; Tables 2 and 3, respectively.

The removal ratio of paracetamol increased with high temperature as appear in results. This refers to the process is endothermic in nature of. A pre-study by [23] proves that rise temperature cause increasesorbent mobility. Other studies by [24] founded that higher

### Table 2: The distribution coefficients of different temperatures.

| k_d   | R²   |
|-------|------|
| 298k  | 303k | 308k | 313k | 318k |
| 3.825 | 4.215| 8.281| 14.748| 29.303| 0.953|

### Table 3: The thermal parameters of paracetamol sorption on the rice husk.

| ΔH(J/mol) | ΔS(J/molK) | ΔG(kJ/mol) |
|-----------|------------|------------|
| 84.803    | -293.817   | 298k       |
|           |            | 303k       |
| 87.642    | 89.111     | 308k       |
|           |            | 90.580     |
| 92.049    | 93.519     | 313k       |
|           |            | 318k       |
temperatures can be attributed with the expansion of pore size of the sorbent. Subsequently, in this test; it possible to say; thereason behind the increment in removing of paracetamol when the temperature is high was because excess mobility of paracetamol magnification of rice husk pore and surface. The small increase in theremoval ratio is prospect because rice husks have usually retains its beginning temperature. This is based on research behaved by [25] which declared that the increase in removing is no longer noticeable because the substitute of deceit if the temperature overrun the beginning. This indicates that the sorption of PC is favored at high temperatures and endothermic in natural; and so that the sorption extent increased with rising temperature. Similar result was reported by [26, 27].

3.4 Isotherm Models of Sorption
Langmuir and Freundlich models was utilized in the research; the isotherms represented the quantity of solute adsorbed at equilibrium per unit weight of sorbent, x/m(mg/g), to the concentration of sorbate at equilibrium, Ce(mg/L). The model of Langmuir shows one of the theories of treating of nonlinear sorption and proposes that the uptake happens on a homogenous surface by monolayer sorption with no reaction between the molecules of sorbed. Langmuir linear unite isotherm is appeared in Eq. (4) [28]:

\[
\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \tag{4}
\]

Where: \(q_e\) is the metal ions of sorbed by biomass (mg/g), \(qm\) is the maximum capability of sorption for monolayer coverage (mg/g), \(b\) is the constant concerning to the binding site affinity (L/mg), and \(Ce\) is metal ions concentration in the solution at equilibrium (mg/L). The constant for equilibrium of adsorbate-adsorbent and the monolayer capacity \(b\) and \(q_e\) were identified from the slope and intercept of the Langmuir plot (Figure 4a).

The Freundlich model may apply for non-ideal sorption on heterogeneous surfaces having multilayer sorption. The linear isotherm of Freundlich model is shown as [28]:

\[
\log q_e = \log K + \frac{1}{n} \log C_e \tag{5}
\]

Where: \(K\) is the constant that determines the proportional capacity of adsorption of the adsorbent (mg/g). a constant \((1/n)\) is determines the intensity of sorption. Both \(K\) and \(n\) were an indication of the adsorption extent and the degree of non-linearity between solution and concentration, sequentially. The plots of linear Freundlich constituted by plotting log \(q_e\) against log \(Ce\) from which the coefficients of adsorption may be estimated (Figure 4b). All constants identified from Langmuir and Freundlich isotherms are given in Table 4.
Figure 4. Isotherm Model of Sorption; (a) Langmuir; (b) Freundlich

Table 4. Parameters of Isotherm forms.

| Parameters          | Langmuir coefficients | Freundlich coefficients |
|---------------------|------------------------|-------------------------|
| \( R^2 \)           | 0.757                  | 0.690                   |
| \( q_m \)           | 2.347                  | n                       |
| \( B \)             | 0.0455                 | K                       |

In comparison by experiential isotherms with the theoretical isotherm models appeared that equation Langmuir is suitable for the experiential data for paracetamol.

3.5 Kinetic Models of Sorption

Studies of kinetic sorption were carried out at (25±2°C); pH7, and 200rpm, where the solution of paracetamol mixed with rice husk (about 4.5g) in glass vials. The mechanism of kinetic parameters data of sorption was examined methodically utilized pseudo first-order, and pseudo second-order models, sequentially[22, 28]:

\[
\ln \left( \frac{q_t}{q_{eq}} \right) = \ln \frac{q_{eq}}{q_t} - k_1 t \\
\frac{t}{q_t} = \left( \frac{1}{k_2 q_{eq}} + \frac{t}{q_{eq}} \right)
\]

Where: \( q_{eq} \) and \( q_t \) (both in mg g\(^{-1}\)) are the amount of paracetamol adsorbed at equilibrium and at time correspondingly. \( k_1 \) (min\(^{-1}\)) and \( k_2 \) (g mg\(^{-1}\) min\(^{-1}\)) are the kinetics rate constants for the Pseudo first and second-order models, correspondingly. Figure 5 and Table 5 showed the results below:
Figure 5. Kinetic Models of Sorption; (a) pseudo-1st-order; (b) pseudo-2nd-order

Table 5. Parameters of Kinetic Models.

|                          | Pseudo-first-order | Pseudo-second-order |
|--------------------------|--------------------|---------------------|
| q<sub>experimental</sub> | k<sub>1</sub> 1/min| q<sub>calculated</sub> | R<sup>2</sup> | k<sub>2</sub> | q<sub>calculated</sub> | R<sup>2</sup> |
|                          | 1.31               | -0.015              | 0.647         | 0.803         | 0.150               | 1.33            | 0.995           |

From Table 5 it found that the theoretic values of q<sub>e</sub>(cal) accepted well with the experiential uptake values, q<sub>e</sub>(exp) if pseudo-second-order model. Moreover, the relation coefficient (R<sup>2</sup>) was 0.995, suggesting that this sorption procedure can characterize using pseudo-second-order process.

3.6 Analysis of FTIR

For initial and qualitative analysis for the basic functional groups that could be existing in the sorption of paracetamol on rice husk waste, an analysis of FTIR-ATR in the solid phase of rice husk was carried out by a Fourier Transform Infrared Spectrometer. Figure 6 appears the result of this analysis.
Figure 6. Analysis of FTIR

The results appeared that paracetamol could be adsorbed by H and O atoms of hydroxyl and carboxylic bonds, which transferred bands to lower frequencies. The reason of these changes may be the cause of the differences in the anti-hydroxyl antagonists, carboxylic acids, alcohol, carboxyl and carbonyl. The results indicate that groups of hydroxyl groups have shifted to a lower frequency. Total displacement of these functional groups was because of the biosorption of paracetamol onto the surface of biomass.

Conclusion
From the results of this research we conclude that rice husks are considered an effective sorbent to remove paracetamol from wastewater by sorption process. These rice husks are available and low cost. Adsorption capacity was highest at pH 7 and from the modeling calculations found Pseudo-second order equation and Langmuir model were best suited for data experience. At high temperatures, the removal efficiency has increased; which means that the reaction is therefore endothermic in natural.

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