Adsorption of phenol from aqueous solution onto Luffa Cylindrica Cords: equilibrium, kinetic, and thermodynamic study

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Abstract: The results obtained show that Luffa cylindrica cords / phenol have an adsorption capacity (qm = 2.54 mg/g). The adsorption process was rapid and reached equilibrium in 25 min of contact at 23 °C and pH 8.5. The different adsorption models Langmuir, Freundlich, Temkin and Elovich were used for the mathematical description of the adsorption equilibrium, and it was found that the very well-equipped experimental data for the Langmuir model (R² = 0.994), the pseudo-first order and pseudo-second-order kinetic models were applied to the experimental data. The experimental data fitted very well the pseudo-second-order kinetic model (R² = 0.999) and also followed the model of intra-particle diffusion (Kdif vary from 0.125 to 0.374 mg/g.min1/2 for concentrations between 10 and 100 mg/L), whereas diffusion is not the only rate control step. Finally, the thermodynamic constants of adsorption phenomena, ∆H° and ∆S° were found to be -6.219 kJ/mol and -0.019 kJ/mol.K in the range of 3 – 23 °C respectively. The negative value of the Gibbs free energy (DS° demonstrates the spontaneous nature of phenol adsorption onto Luffa cylindrica cords.

Key Words: Adsorption, phenol; Kinetic; thermodynamics; biomass.

I. Introduction

Heavy metal pollution is an environmental problem of worldwide concern. The heavy metals are among the most common pollutants found in industrial effluents [1]. Chrome is one of toxic heavy metals and it can be present in wastewater from electroplating, refining and welding industries [2]. The chronic toxicity of chrome to humans and the environment has been well documented and high concentration of chrome causes cancer of lungs, nose and bone [3]. Several processes have been employed for the removal of chrome ions from water and wastewater including chemical precipitation, ion-exchange, membrane filtration, electrochemical treatment and adsorption [4]. Wastewaters containing phenolic compounds are a serious environmental problem, and these waters cannot simply be released into the environment without treatment.

The discharge of wastewater containing large amounts of organic contaminants represents a serious risk to the general population [1]. Wastewater containing organic contaminants such as phenolic compounds implies serious discharge problems, due to their poor biodegradability, high toxicity, and possible accumulation in the environment [2]. Phenols are introduced into surface water from industrial effluents, such as those from plastic, leather, paint, rubber, pharmaceuticals, petrochemicals, and pesticides, among others [3-5]. It is a fact that phenol and its derivatives found in natural water sources represent a serious risk to human health and water quality [6]. Phenolic compounds represent a serious danger because of their high toxicity and carcinogenicity even at low concentrations. In some industries such as food processing, the rejected effluents may contain relatively large amounts of substances (phenolic) so that the aquatic environment is constantly threatened [7]. Indeed, in normal activity, a single refinery can reject up to 0.5 mg/L of phenol while a catalytic cracking unit of oil can reject up to 1 mg/L. the maximal concentration
phenol in water for consumption is 0.001 mg/L in the European standard [7]. Various techniques have been used for phenol removal in the wastewater treatment. In general, these removal techniques are divided into three main categories: physical, chemical and biological [8]. Traditionally, biological treatment, adsorption, reverse osmosis, ion exchange, catalytic oxidation and solvent extraction are the most widely used techniques for removing phenol and related organic substances [8, 9]. Among all of these methods adsorption has been preferred due to its cheapness and the high-quality of the treated effluents especially for well-designed sorption processes [10]. Adsorption by agricultural by-products used recently as an economical and realistic method for removal of different pollutants has proved to be efficient at removing of phenol [11, 12]. Luffa cylindrica cords (LCC), mainly consists of cellulose, hemicelluloses and lignin; of composition (60%, 30% and 10% by weight, respectively) [13]. Cellulose structure consists of monomeric unit of a β - D - glucopyranose linked through 1,4-glucosidic linkage. Cellulose is renewable, cheap and low in density, exhibits better processing flexibility and is a biodegradable material. Cellulose is a highly functionalized, linear stiff chain homopolymer, characterized by its hydrophilicity, chirality, biodegradability and broad chemical modifying capacity [14]. Because of its unique structure, Luffa cylindrica, has been used as an efficient adsorbent or as a carrier for immobilization of some microalgal cells for the removal of water pollutants [15, 16]. For the present study, a batch - contact - time method was used, and the equilibrium of phenol adsorption onto Luffa cylindrica cords were investigated with the attempts to fit the data to Langmuir, Freundlich, Temkin and Elovich equations. The uptake of phenol on Luffa cylindrica cords were examined as a function of temperature, initial phenol concentration, adsorbent dose, pH, and contact time. The adsorption kinetic data of the biomaterial were tested by the pseudo - first - order and the pseudo - second - order kinetic models. The thermodynamics of the adsorption was also evaluated.

II. Materials and methods

II.1. Preparation of biosorbent

The vegetable sponge of Luffa cylindrica cords (LCC), an natural product which grows in the north of Algeria. The pre-treatment of the sponges consisted of cooking with boiling water for 30 min followed by washing with distilled water in order to remove the seeds and loose cord fragments. These cords were then placed in a solution of NaOH (12%) for 15 min and washed again with tap water. They are whitened with bleach 12% for 3 h at ambient temperature after which the cords are rinsed. At pH >8.5, the decrease of phenol adsorption may have resulted from the following reasons. Similar with distilled water several times. The cords of LCC were oven dried at 105 °C for 120 min, then crushed and sifted by standard sifting and crushing.

II.2. Preparation of solution

Phenol used in this study was obtained from Shanghai Chemical Co., Ltd. (analytical grade). Stock solution was prepared by weighing out the pure crystalline solid in solution of sodium bicarbonate 0.1 N for phenol. The test solutions were prepared by diluting some stock solution up to the desired concentration. The ranges of concentrations of phenol prepared from stock solution varied between the values of 10 and 100 mg/L. The pH of each solution was adjusted to the required value pH = 8.5 with the 0.1 N sodium bicarbonate.

II.3. Methods of adsorption studies

Batch adsorption studies were conducted by shaking the flasks for a period of time using an air bath mechanical shaker. The experimental process was as followings: put a certain quantity of LCC into conical flasks, then, added the phenol solution in single component system, vibrated sometime at a constant speed of 350 rpm in a shaking air bath. After a period of shaking and contact time, took out the conical flasks, filtrated to separate LCC powders and the solution. The phenol concentration analysis of filtrate solution was immediately measured with UV-visible spectrophotometer ((Unicam 8625, France)) at 270 nm wavelength. The phenol adsorption capacity (qe, mg/g) was determined as follows:

\[ q_e = \frac{(C_0 - C_t) V}{m} \]  

(1)

Where q_e is the amount of phenol taken up by the adsorbent (mg/g); C_t (mg/L) is the concentration of phenol solution at time, t (min), C_0 (mg/L) is the initial concentration of phenol. V and m are the volume of the solution (L) and the mass of the adsorbent (g), respectively.

III. Results and discussion

III.1. Effect of pH on the removal of phenol

The effect of solution pH in the range from 2 to 12 on phenol adsorption is shown in Figure 1. As seen, the removal decreased from about 78% to 58% when pH decreased from 2 to 12. The removal of phenol by LCC was highly dependent on pH. The phenol removal increases with pH from 2.0 to 8.5, then sharply decreases at pH >8.5. The maximum adsorption is attained at pH of 8.5. At pH 2.0, there are many positive charges on the surface of LCC, which give a large static repulsion force. As pH increases from 2.0 to 8.5 the static repulsion force decreases and the phenol adsorption increases. These results have been reported by other groups such as Abdelwahab et al. [12] and Nadavala et al. [17].
III.2. Effect of adsorbent dose

These experiments gave the effect of solid/liquid ratio on the adsorption efficiency at equilibrium (Figure 2). The results demonstrated, for the selected sawdust and in presence of 100 mg/L of initial phenol concentration that the phenol adsorption capacity did not change significantly for a solid/liquid ratio higher than 3.33 g/L. In fact, the adsorption capacity obtained with 0.83 g/L of solid/liquid ratio was 0.82 mg/g; however, for 1.7, 2.5 and 3.33 g/L respectively. Similar results were previously reported by some researchers [18].

Figure 3. Effect of absorbent dosage on the phenol adsorption onto LCC: V=300 ml, T=23°C.

A rapid adsorption is observed at the beginning and then a spreading with saturation, A rapid increase in the adsorption capacity of the phenol occurs within a few minutes (12 min), due to the adsorption of phenol to the surface of the particles of each adsorbent. This first phase constitutes the essential part of the phenomenon of adsorption because the kinetics of fixation is limited by the low residual concentration of phenol. In the second stage, the occupation of deep adsorption sites requires diffusion of the adsorbate within the micropores of the adsorbent, Similar results have been reported by other groups such as Cherifi et al. [19] and Afsharnia et al. [20].

III.3. Effect of contact time on phenol adsorption

The results obtained from the Adsorption rate tests are shown in Figure 3, the evolution of the adsorbed quantity of phenol per gram of LCC as a function of the contact time at initial concentration 100 mg/L as a phenol, showing that the amount of adsorbate fixed on each material increases with the increase of the content of the solution in phenol.

Figure 4. Effect of temperature on the amount adsorbed by the LCC / phenol pH 8.5.

A rapid adsorption is observed at the beginning and then a spreading with saturation, A rapid increase in the adsorption capacity of the phenol occurs within a few minutes (12 min), due to the adsorption of phenol to the surface of the particles of each adsorbent. This first phase constitutes the essential part of the phenomenon of adsorption because the kinetics of fixation is limited by the low residual concentration of phenol. In the second stage, the occupation of deep adsorption sites requires diffusion of the adsorbate within the micropores of the adsorbent. Similar results have been reported by other groups such as Cherifi et al. [19] and Afsharnia et al. [20].

III.4. Effect of temperature

The temperature is well known to play an important role in the adsorption process [21]. The adsorption capacity for the system (Phenol / LCC) increases with increasing the temperature from 4 to 23 °C. The best removal efficiency (2.54 mg/g and 84%) was obtained at a temperature of 23°C (Figure 4). Similar of the adsorption process has been reported for other adsorbent systems [7, 11, 22].

III.5. Adsorption Equilibrium Study

Adsorption isotherms describe the theoretical adsorption maximum capacity of quantitative adsorbents, and determined the feasibility of adsorbent dosage; however, they serve as important reference values in the design process of the adsorption system.
In this study, the adsorption isotherms were plotted using the Langmuir, Freundlich, Temkin and Elovich model [23]. The Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites, using uniform strategies of adsorption [24]. The linear form of the Langmuir isotherm equation is given as:

\[
\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}
\]

(2)

Where \( C_e \) is the equilibrium concentration of the adsorbate (mg/L), \( q_e \) is the sorption capacity of adsorbent (mg/g), \( q_m \) and \( K_L \) are the maximum phenol adsorbed per unit mass of the adsorbent (mg/g) and Langmuir constant, in relation to energy of sorption which quantitatively indicates the affinity between the adsorbent and phenol (L/mg), respectively [25].

The favorable or unfavorable of the adsorption system can be determined based on the essential characteristic of the Langmuir model which can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, RL, which is defined as follows:

\[
R_L = \frac{1}{1 + K_L C_0}
\]

(3)

The value of RL indicates the shape of isotherm to be either unfavorable (RL > 1), linear (RL = 1), favorable (0 < RL < 1) or irreversible (RL = 0) [26].

The Freundlich equation can be linearized in a logarithmic form for the determination of the Freundlich constants as follows [27]:

\[
Ln(q_e) = Ln\left(k_F n_F\right) + \frac{1}{n_F} Ln\left(C_e\right)
\]

(5)

Where \( k_F \) (mg1+1/nL/g), \( L1/n \) and \( l/n_F \) are the adsorption constants of Freundlich model generally related to the strength of interaction between adsorbate and sorbent. They can be determined from the plot of Ln (qe) vs Ln (Ce) [28, 29].

Temkin’s model rests on the assumption that during the adsorption gas phase, the heat of adsorption due to interactions with the adsorbate decreases linearly with the recovery rate \( \theta \). From \( q_e \) plotted as a function of \( Ln\; C_e \), BT, and KT values can be determined [30]:

\[
q_e = \frac{RT}{B_T} Ln\left(K_T \cdot C_e\right)
\]

(6)

Where \( R \) is the perfect gas constant (8.314 J/mol.K), \( T \) is the absolute temperature (°C), \( BT \) is the variation in energy of adsorption (J/mol), and \( KT \) is the constant of Temkin (L/mg).

Elovich equation is also used successfully to describe second order kinetic assuming that the actual solid surfaces are energetically heterogeneous, but the equation does not propose any definite mechanism for adsorbate-adsorbent [31]. It has extensively been accepted that the chemisorption process can be described by this semi-empirical equation [32]. The linear form of this equation is given by [31]:

\[
q_t = \frac{1}{\beta_E} Ln\left(\alpha_E \beta_E\right) + \frac{1}{\beta_E} Ln\left(t\right)
\]

(7)

Where \( \alpha_E \) is the initial adsorption rate (mg/g.min), and the parameter be is related to the extent of surface coverage and activation energy for chemisorption (g/mg). The Elovich coefficients could be computed from the plots \( q_t \) vs \( Ln\; t \). The initial adsorption rate, and the desorption constant, \( \beta_E \), were calculated from the intercept and slope of the straight-line plots of \( q_t \) against \( Ln\; t \).

The plots of \( Ce/qe \) vs. \( Ce \) for the adsorption of phenol at 4, 17, and 23 °C according to the linear form of the Langmuir isotherm is shown in Figure 5.

Table 1 summarizes the constants of the Langmuir, Freundlich, Elovich and Temkin isotherms obtained from the slope and the interception of the plots of each isotherm at different temperatures. The values of \( R^2 \) exceed 0.9 for the two models of Langmuir and Freundlich, suggesting that the two models with near experimental results.

Figure 5 shows the Langmuir plot for the adsorption of phenol onto LCC at 4, 17 and 23 °C, as reproduced by the linearized Langmuir (2), and the best straight lines representing the fitted points. Hence, it is evident that the equilibrium data are accommodated well by the Langmuir model, with high correlation coefficients, as shown in Table 1. Such coefficients are indicative of monolayer coverage of the phenol at the outer surface of the LCC particles, and with maximum adsorption capacity (Table 1). The results of Table 1 also show that an increase in temperature from 4 to 23 °C promoted an increase in the adsorption capacity.

Similar results were found for the adsorption of phenol onto Luffa cylindrica cords shells [22].
Table 1. Parameters of different adsorption models for phenol / LCC

<table>
<thead>
<tr>
<th>Isotherm model</th>
<th>Parameter</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$K_F$ (mg/$^{1+1/n}$g.L$^{-1/n}$)</td>
<td>0.180</td>
</tr>
<tr>
<td></td>
<td>$1/n_F$</td>
<td>0.081</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.960</td>
</tr>
<tr>
<td>Langmuir</td>
<td>$q_m$ (mg/g)</td>
<td>0.236</td>
</tr>
<tr>
<td></td>
<td>$K_L$ (L/g)</td>
<td>1.35</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.996</td>
</tr>
<tr>
<td></td>
<td>$R_L$</td>
<td>0.007</td>
</tr>
<tr>
<td>Temkin</td>
<td>$K_T$ (L/g)</td>
<td>1159.16</td>
</tr>
<tr>
<td></td>
<td>$B_T$ (J/mol)</td>
<td>1072.774</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.450</td>
</tr>
<tr>
<td>Elovich</td>
<td>$\alpha_{El}$ (mg/min.g)</td>
<td>536.932</td>
</tr>
<tr>
<td></td>
<td>$\beta_{El}$ ($[g/mg]$)</td>
<td>34.83</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.547</td>
</tr>
</tbody>
</table>

According to the $R_L$ values, all the systems correspond to favorable adsorption processes (Table 1). The values tended toward zero, representing the ideal irreversible case, rather than toward unity, representing the completely reversible case [33].

By comparison of the results obtained in this study with those in the previously reported works (Table 2) on adsorption capacities of various low-cost adsorbent in aqueous solution for Phenol, it can be stated that our findings are extremely good.

Table 1. Previously reported adsorption capacities of various adsorbents for phenol

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>$q$ (mg/g)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw Moroccan Pyrophyllite</td>
<td>11.22</td>
<td>[34]</td>
</tr>
<tr>
<td>Luffa cylindrica fibers</td>
<td>0.97</td>
<td>[12]</td>
</tr>
<tr>
<td>Granular activated carbon</td>
<td>213</td>
<td>[35]</td>
</tr>
<tr>
<td>Organic-inorganic hybrid mesoporous material</td>
<td>11</td>
<td>[36]</td>
</tr>
<tr>
<td>Water hyacinth ash</td>
<td>6.4</td>
<td>[37]</td>
</tr>
<tr>
<td>FCM (Fibers gourds Mexican)</td>
<td>0.69</td>
<td>[11]</td>
</tr>
<tr>
<td>Date stones</td>
<td>48.71</td>
<td>[38]</td>
</tr>
<tr>
<td>Sugarcane bagasse fly ash</td>
<td>23.832</td>
<td>[39]</td>
</tr>
<tr>
<td>Luffa cylindrica cords</td>
<td>2.54</td>
<td>This study</td>
</tr>
</tbody>
</table>

II.6. Adsorption Kinetics

Pseudo - first - order kinetic model was set forth by Lagergren in 1898 [40]. This model is not applicable for a total adsorption period for many instances. It can be generally used for the first minutes of adsorption procedure in other words for the periods before reaching equilibrium. This adsorption rate can be expressed by the equation.

$$\frac{dq}{dt} = k_1(q_e - q_t)$$

(8)

The integrated form of the Lagergren equation is given by:

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303}t$$

(9)

Where $q_e$ and $q_t$ are the amounts adsorbed at equilibrium and at time, $t$ (mg/g), and $k_1$ is the rate constant of the pseudo - first - order adsorption (min$^{-1}$).

The pseudo-second-order kinetic model (10) is another model used in the analysis of adsorption kinetics. Contrary to the pseudofirstorder kinetic model, this model is compatible with the mechanism of rate-controlling step throughout the adsorption. The pseudo - second-order kinetic model is given by the following equation [41]:

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}t$$

(10)

Where $k_2$ is the rate constant of the pseudo-second order adsorption (g/mg.min$^{-1}$).

The kinetics of adsorption of the adsorbate on the adsorbent was verified at different initial concentrations (10, 60 and 100 mg/L).
The validity of each model was determined by the sum of squared errors (SSE), given by:

\[ SSE = \frac{1}{N} \sum_{N} (q_{e,exp} - q_{e,cal})^2 \]  

(11)

where N is the number of trials. Low value indicates a better SSE smoothing.

The intraparticle diffusion parameter, \( k_{\text{diff}} \), is defined by the following equation [42]:

\[ q_{t} = k_{\text{diff}} t^{1/2} + C \]  

(12)

Where \( k_{\text{diff}} \) is the intraparticle diffusion constant (mg/g.min\(^{1/2}\)), and \( C \) is the intercept. The intraparticle diffusion plots of the experimental results, \( q_{t} \) versus \( t^{1/2} \) for different initial phenol concentrations at 23 °C.

The kinetic parameters for adsorption of phenol presented in Table 3 were calculated from plots of log (\( q_{t} - q_{0} \)) vs. t and the plots of \( t/q_{t} \) vs. t.

### Table 3. Pseudo - first - order and Pseudo - second - order kinetic parameters for the adsorption of phenol onto LCC.

<table>
<thead>
<tr>
<th>Kinetic model</th>
<th>Phenol (mg/L)</th>
<th>10</th>
<th>60</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pseudo - first - order kinetic model</strong></td>
<td>q_{e,exp} (mg/L)</td>
<td>0.65</td>
<td>1.35</td>
<td>2.54</td>
</tr>
<tr>
<td></td>
<td>q_{e,cal} (mg/g)</td>
<td>0.521</td>
<td>0.524</td>
<td>0.188</td>
</tr>
<tr>
<td></td>
<td>K_{1} (min(^{-1}))</td>
<td>0.051</td>
<td>0.046</td>
<td>0.053</td>
</tr>
<tr>
<td></td>
<td>R(^2)</td>
<td>0.601</td>
<td>0.881</td>
<td>0.681</td>
</tr>
<tr>
<td></td>
<td>SSE (%)</td>
<td>4.62</td>
<td>27.53</td>
<td>78.40</td>
</tr>
<tr>
<td><strong>Pseudo - second - order kinetic model</strong></td>
<td>q_{e,cal} (mg/g)</td>
<td>0.855</td>
<td>1.383</td>
<td>2.564</td>
</tr>
<tr>
<td></td>
<td>K_{2} (g/mg.min)</td>
<td>1.375</td>
<td>0.352</td>
<td>0.364</td>
</tr>
<tr>
<td></td>
<td>R(^2)</td>
<td>0.999</td>
<td>0.999</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>SSE (%)</td>
<td>6.83</td>
<td>1.10</td>
<td>0.80</td>
</tr>
<tr>
<td><strong>Intraparticle diffusion</strong></td>
<td>K_{diff} (mg.g.min(^{-1}))</td>
<td>0.125</td>
<td>0.203</td>
<td>0.374</td>
</tr>
<tr>
<td></td>
<td>C (mg/g)</td>
<td>0.109</td>
<td>0.113</td>
<td>0.307</td>
</tr>
<tr>
<td></td>
<td>R(^2)</td>
<td>0.978</td>
<td>0.918</td>
<td>0.871</td>
</tr>
</tbody>
</table>

For the first - order kinetic model, the obtained \( R^2 \) values were relatively low, ranging from 0.601 to 0.881, and the calculated \( q_{\text{cal}} \) were much larger than the experimental \( q_{\text{exp}} \). The pseudo - second - order rate constant \( k_{2} \) and the corresponding linear regression correlation coefficient values, \( R^2 \), are given in Table 3. The applicability of the kinetic model is compared by judging the correlation coefficients \( R^2 \) and the agreement between the calculated and the experimental \( q_{e} \) values. In a view of these both considerations, we may conclude that the pseudo second-order mechanism is predominant \( R^2 \) (0.999). Similar results have been reported by other groups such as Uddin et al. [37] and Kayode et al. [43].

We observe that the diffusion rate constants increase in the same direction as the initial concentration of phenol, Table 3. Indeed for initial concentrations between 10, 60 and 100 mg/L, the values of \( K_{\text{diff}} \) vary from 0.125 to 0.374 mg/(g.min\(^{1/2}\)) for the Phenol / LCC system. According to the study of Gundogdu et al. [44] on the diffusion intraparticle for the Phenol / Low-Cost Activated Carbon system, the value of \( K_{\text{diff}} \) is equal 0.5657 mg/g/min\(^{1/2}\). So we note that the coefficient \( k_{\text{diff}} \) is 1.52 times greater than that of \( K_{\text{diff}} \) found by Gundogdu et al. [44] to the concentration \( C_{0} = 100 \) mg/L.

**II.7. Adsorption thermodynamics**

Figure 9 shows just such a plot with a correlation coefficient of 0.720 (Table 4). The \( \Delta H^0 \) and \( \Delta S^0 \) values are thus found to be - 6.219 kJ/mol and - 0.019 kJ/mol.°C, respectively, while the \( \Delta G^0 \) values are - 0.337, - 0.457, and - 0.715 kJ/mol.°C. The negative \( \Delta G^0 \) values indicate the feasibility and spontaneous adsorption.
nature of the adsorption process with a high preference of phenol on LCC [48]. The \(\Delta H^0\) for phenol adsorbed onto LCC was negative (-6.129 kJ/mol), indicating that the adsorption was exothermic. The \(\Delta S^0\) for phenol adsorbed onto LCC was -0.019 kJ/mol.°C The negative value of \(\Delta S^0\) suggested decrease in degree of freedom of the adsorbed phenol [49]. Adsorption processes with \(AG^0\) values in the -20 to 0 kJ/mol range correspond to spontaneous physical processes, while those with values in the -80 to -400 kJ/mol range correspond to chemisorption [50]. As \(\Delta G^0\) changed from -0.337 to -0.715 kJ/mol when the temperature increased from 4, 17, and 23 °C, it can be concluded that the adsorption mechanism is dominated by physisorption, in keeping with the finding that the adsorption is rapid and more spontaneous at higher temperature. Spontaneous adsorption processes are a common feature of many other studies of this sort [51]. Similar results were reported in the literature for the adsorption of phenol by organomontmorillonit [52], the adsorption of phenol onto chemically modified activated carbon [53] and adsorption of phenol onto Luffa cylindrica fibers [12].

Figure 9. Relationship between Langmuir sorption equilibrium constant and temperature for phenol / LCC; \(C_0= 100\) mg/L.

Table 4. Thermodynamic parameters for the adsorption of phenol onto LCC different temperatures

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>(\Delta G^0) (kJ/mol)</th>
<th>(\Delta H^0) (kJ/mol)</th>
<th>(\Delta S^0) (J/mol.K)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>-0.715</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>-0.457</td>
<td>-6.219</td>
<td>-0.019</td>
<td>0.720</td>
</tr>
<tr>
<td>23</td>
<td>-0.337</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

III. Conclusions
Kinetic, Equilibrium, and thermodynamic studies were made for the adsorption of phenol from aqueous solution onto LCC powder at pH 8.5. Results of adsorption showed that LCC can be effectively used as a biosorbent for the removal of phenol. The kinetics studies of Phenol on LCC indicated that the adsorption kinetics of phenol on LCC followed the pseudo - second - order at different concentration values. The equilibrium data have been analyzed. The results showed that the phenol followed Langmuir isotherm. Thermodynamic studies indicated that the phenol adsorption onto LCC was a spontaneous, exothermic, and physical reaction. Based on the data of present study, LCC, an inexpensive and easily available material, can be an alternative for costlier adsorbents used for phenol removal in wastewater treatment processes.

IV. References


Please cite this Article as: