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# Biosorption of phenol from aqueous solutions by the *Aspergillus niger* biomass: comparison of linear and non-linear regression analysis

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ABSTRACT

In this study, the removal characteristics of phenol from aqueous solution by the live *Aspergillus niger* were investigated under various operating variables like contact time, initial phenol concentration, biomass dosage, and temperature. The biosorption of phenol reached equilibrium in 48 h. The maximum loading capacity of the sorbent was also found to be 30.0 mg/g for live *A. niger* at an initial phenol concentration of 550 mg/L. Kinetic evaluation of experimental data showed that the biosorption of phenol on *A. niger* conformed closely to the intra particle diffusion model. Langmuir and Freundlich models were applied to describe the biosorption isotherms. Akaike's information criterion (AIC) values were calculated for Langmuir (6.54) and Freundlich (12.45) isotherms, respectively. Having a smaller AIC value suggests that Langmuir isotherm is more likely to be a better fit. Thermodynamic parameters such as standard Gibbs free energy ($\Delta G^{\circ}$), standard enthalpy ($\Delta H^{\circ}$), and standard entropy ($\Delta S^{\circ}$) were obtained by applying the Van't Hoff equation. The thermodynamics parameters indicated that the biosorption was spontaneous and endothermic. This research showed that fungal biosorption has a potential to be used in the removal of phenol from wastewaters.

*Keywords: Aspergillus niger*; Biosorption; Equilibrium isotherm; Kinetics; Phenol

## 1. Introduction

The removal of organic contaminants from groundwater has become the major focus of research and policy debate on separation of contaminants contained in polluted waters. This is because their presence even at low concentrations can prove an impediment to the use (and/or) reuse of water [1]. Phenols are among the most common pollutants of wastewater that require careful treatment before they are discharged into the receiving body of waters [2]. Phenolic compounds are highly toxic, and many are known or suspected human carcinogens. Because of their toxicity, the US Environmental Protection Agency (EPA) and the European Union have designated phenols as priority pollutants [3]. EPA regulations call for lowering phenol content in the wastewater to less than 1 mg/L [4]. Loss of

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appetite, headache, rapid fatigue, and severe chronic insomnia are reported as symptoms of chronic phenol toxicity in humans after long-term intake of high phenol concentrations [5].

Many industries use phenolic materials in their manufacturing processes. Phenolics are present in the wastewaters of industries such as coking, synthetic rubber, pharmaceuticals, oil and gasoline, paper, textiles, wood, etc. Their concentrations range from trace quantities to 1,000 μg/L; these levels are present even in municipal wastewaters. There have been reports of toxic organic compounds remaining in trace quantities (μg/L) in the treated effluents of many wastewater treatment plants [6]. Phenols, as a class of organics are similar in structure to the more common herbicides and insecticides in that they are resistant to biodegradation [3]. Phenol is harmful to organisms and is the cause of significant taste and odor problems in drinking water even at concentrations as low as 1 μg/L [7].

In recent years, increasing concern for public health and environmental quality has led to the establishment of rigid limits on the acceptable environmental levels of specific pollutants. Thus, the removal or destruction of phenols from process or waste streams has become a major environmental problem [3]. Several methods such as biological treatment [8], adsorption, precipitation, ion change, solvent extraction [4], chemical oxidation, photo degradation, coagulation–flocculation [2], etc. are among those most widely used for removing phenols and their derivatives from wastewater.

Biosorption by biological treatment methods, in particular, is a well-established technique for the removal of low concentrations of organic and other pollutants from large volumes of potable water, process effluents, wastewater, and aqueous solutions [3]. The interest in the potential utilization of fungal biomass as a biosorbent is increasing due to the need for economical and efficient adsorbents to remove organic contaminants from wastewater by adsorption or a related process, even in the absence of physiological activity [9].

The concept of biosorption may involve several chemical processes such as adsorption, ion exchange, and covalent bonding with the biosorptive sites of the micro-organisms including carboxyl, hydroxyl, sulphydryl, amino, and phosphate groups. Fungal cell walls and their components have a major role in biosorption. Fungal biomass can also remove considerable quantities of pollutants from aqueous solutions by adsorption or related processes, even in the absence of physiological activity [5].

This study evaluates the effectiveness of the *Aspergillus niger* biomass for the sorption of phenol and aspects of their environmental stability in aqueous solution. The objectives of this study were: (1) to evaluate the influences of various factors on biosorption, such as sorption time, initial concentration of phenol, temperature, and biomass concentration; (2) to establish a kinetic model that best describes the biosorption of phenol by the live *A. niger* biomass and; (3) to analyze the equilibrium adsorption data using the Freundlich and Langmuir adsorption isotherm and (4) to calculate the thermodynamic parameters such as $\Delta G^{\circ}$, $\Delta H^{\circ}$, and $\Delta S^{\circ}$.

## 2. Materials and methods

### 2.1. Micro-organism and its growth conditions

A fungal strain of *A. niger* (04017) was inoculated into a sterile growth medium comprised of dextrose (20 g/L), peptone (10 g/L), and yeast extract (3 g/L) in distilled water. One hundred milliliters of the medium was transferred to 250-mL conical flasks. The flasks were placed on a rotary shaker operating at 125 rpm. *A. niger* was thus cultured aerobically. All culture works were conducted under aseptic conditions at 25°C. Growth of the fungus was monitored after two days and it was observed that the growth was in the form of pellicles. In the days that followed the pellicles increased in diameter. The resulting biomass was harvested from the incubation medium by centrifugation after four days of growth, and washed thoroughly with deionized water to remove the growth medium adhering to its surface [6,8,10]. This washed biomass is hereafter referred to as "live biomass" [11]. After centrifugation under the same conditions, we were sure that the wet biomass that was used for further biosorption studies had equal amounts of water content.

### 2.2. Chemicals

Phenol (>99.0% purity) was obtained from Carlo Erba, and was used without further purification. Stock solutions of phenol were prepared by dissolving 1.0 g of the phenol in 1 L of distilled water. All the test solutions were prepared by diluting the stock solution of the phenol compound to the desired concentration. All solutions were stored in the dark at 4°C prior to use.

### 2.3. Biosorption experiments

Batch kinetic studies were conducted with the live *A. niger* biomass at a temperature of 28°C to determine the equilibrium time. The biomass ranging from 0.25 to 1.00 g was added in increments of 0.25 g to 100 mL of

the phenol solution at a known concentration stored in the 250-mL conical flasks. All phenolic solutions were studied at a natural pH (5 and 6) because of maximum efficiency [12]. The flasks were then immediately covered to prevent the loss of phenol by volatilization. They were then placed on a rotary shaker set at 125 rpm. Samples were drawn at regular intervals up to the point where equilibrium was reached. These samples were filtered through 0.45-μm cellulose acetate membrane filters. The supernatant was then analyzed by spectrophotometer (T70 UV/vis Spectrometer) for assessing the remaining phenol compound using a direct photometric method (Method 5530) according to Standard Methods [13]. All the experiments were conducted in duplicate and sometimes repeated further, and the mean values were used in the analysis of data. The amount of phenol adsorbed was calculated using the following Eq. (1) [14]:

$$q_t = (C_o - C_t)V/m \quad (1)$$

where $q_t$ (mg/g) is the amount of phenol adsorbed on the biosorbent at any given time (h), $V$ (mL) is the volume of the solution, $C_o$ (mg/L) is the initial phenol concentration, $C_e$ (mg/L) is the final concentration of phenol in the solution at time $t$, and $m$ (g) is the quantity of the biosorbent.

The term used was $q_{eq}$ (the amount of phenol adsorbed on the biosorbent at equilibrium (mg/g)) term instead of $q_t$ which defined biosorption at the equilibrium point.

## 3. Results and discussion

### 3.1. Effect of contact time and biomass dosage

The effect of biomass dosage on the biosorption of phenol on *A. niger* was studied using different biomass dosages in the range 2.5–10.0 g/L (Fig. 1). Results showed that the biosorption efficiency is highly dependent on the increase in biomass dosage of the solution. This is to be expected, because the higher the dose of biomass in the solution, the greater the availability of exchangeable sites for the phenol compound. The maximum biosorption efficiency of the phenol was attained at a biomass dosage of about 10.0 g/L. Therefore, the optimum biomass dosage was selected as 10.0 g/L for further experiments. Dosage further not increased that highly efficiency was reached while at 10.0 g/L biomass dosage.

The contact time was considered one of the most important factors affecting the biosorption efficiency. Fig. 1 also shows the biosorption efficiency of phenol

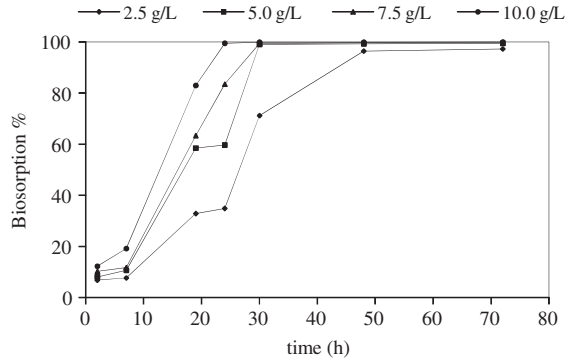


Fig. 1. The effect of biomass dosage and contact time on the biosorption efficiency (natural pH; temperature, 28˚C; phenol concentration, 48 mg/L; agitating rate, 125 rpm and V, 100 mL).

by *A. niger* as a function of contact time and biomass dosage. The biosorption efficiency increases with rise in contact time up to 30 h and from 48 h onwards it remains almost constant. An increase in contact time to 72 h did not show appreciable change, indicating that the sorption process was rapid. Therefore, 48 h was the optimum contact time selected for further experiments.

The variations in the adsorption capacity of phenol compound at different biomass dosage vs. contact time are shown in Fig. 2. Fig. 2 shows that the equilibrium sorption capacity for phenol was influenced by the biomass dosage. Biosorption capacities of the biomass declined with increasing concentration of live *A. niger*. After 24 h, when the biomass dosage was increased from 2.5 to 10.0 g/L, the biosorption capacity of *A. niger* declined from 6.56 to 4.68 mg/g. The maximum loading capacity of the biomass was also found to be 4.70 mg/g at the initial biomass

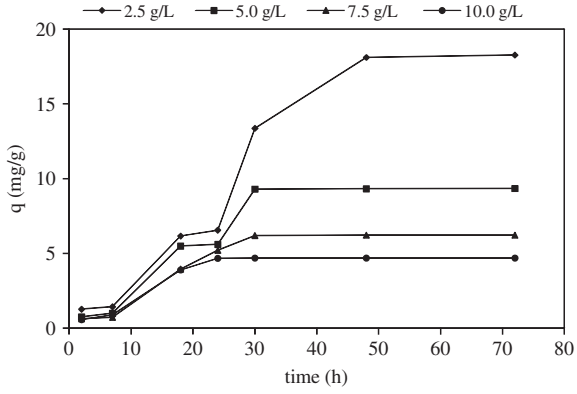


Fig. 2. The effect of biomass dosage and contact time on phenol biosorption (natural pH; temperature, 28˚C; initial phenol concentration, 48 mg/L; agitating rate, 125 rpm and V, 100 mL).

concentration of 10.0 g/L, and 18.28 mg/g for *A. niger* at initial biomass concentration of 2.5 g/L after 72 h.

The drop in biosorption capacity with an increase in biomass dosage was due to the binding sites of the biomass remaining unsaturated during the biosorption reaction. Similar trends were also observed by [7,15,16]. Two possible reasons—the ease of access to chemical binding sites and the competition between the biomass—might explain the decline in sorption capacity when the biomass dosage was increased. The first scenario relates to the opportunity of the phenol molecule to interact with chemical binding sites on the biomass. Since an increase in biomass dosage usually yields a higher biomass density, which brings the microbial cells closer to each other. Consequently, the accessibility of phenol to the active surface area on the sorbents diminishes.

### 3.2. Biosorption kinetics of phenol

In order to investigate the mechanism of phenol biosorption on live *A. niger* and examine the potential rate-controlling step, i.e. mass transfer or chemical reaction, and evaluate the biosorption kinetics of phenol different kinetic models have been used. Three kinetic models from which the best results were obtained; the intra particle diffusion model [17] (Fig. 3(a)), elovich model [18] (Fig. 3(b)), and pseudo-second-order kinetic model [19] (Fig. 3(c)) were used to fit the experimental data at different initial concentrations of *A. niger*.

A series of contact time experiments were carried out with constant phenol concentration of 48 mg/L. The biosorption kinetic model parameters and correlation coefficients are compared in Table 1. As shown in Table 1, the correlation coefficient of the intra particle diffusion model equation is higher than that of the other models. It can be concluded that the intra particle diffusion mechanism is the superior vehicle for the biosorption of phenol compound on live *A. niger*. The values noted in Table 1 show that $k_d$ was lower at a higher initial concentration of *A. niger*.

If intra particle diffusion is involved in the sorption process, a plot of the adsorption uptake vs. the square root of time will result in a linear relationship and thus intra particle diffusion should be the rate-controlling step if the lines were to pass through the origin [19]. Although Fig. 3(a) was shown that there was a linear relationship over a period of time, the graph did not pass through the origin. The reason of this intra particle diffusion was not the only rate-controlling step. The adsorption related with some other mechanisms too might be involved in the biosorption of phenol by live *A. niger*.

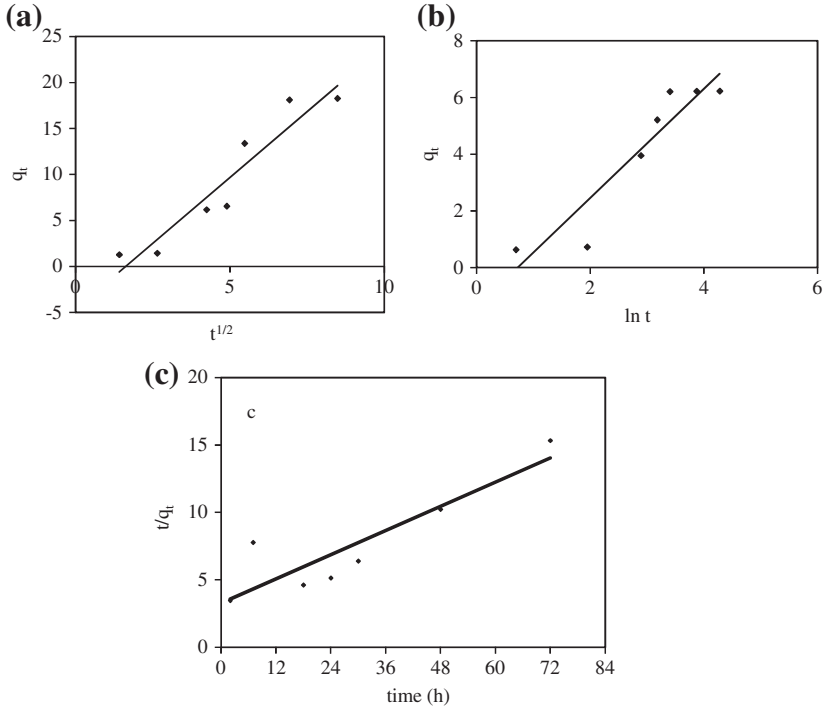


Fig. 3. Intra particle diffusion model (biomass concentrations: 2.5 g/L) (a), Elovich model (biomass concentrations: 7.5 g/L) (b) and pseudo-second-order kinetic model (biomass concentrations: 10.0 g/L) (c).

Table 1
Comparison of kinetic model constants for phenol at different biomass concentrations

| Pseudo-second-order kinetic model | | | |
|---|---|---|---|
| Dose (g/L) | $q_{eq}$ (mg/g) | $k_{2,ad}$ (g/mg/h) | $R^2$ |
| 2.5 | 125.000 | 0.000 | 0.0309 |
| 5.0 | 22.422 | 0.001 | 0.3063 |
| 7.5 | 12.180 | 0.002 | 0.4154 |
| 10.0 | 6.693 | 0.007 | 0.7965 |
| Intra particle diffusion model | | | |
| | $C$ | $k_d$ | $R^2$ |
| 2.5 g/L | 4.637 | 2.866 | 0.9014 |
| 5.0 g/L | 1.200 | 1.445 | 0.8489 |
| 7.5 g/L | 0.416 | 0.942 | 0.8150 |
| 10.0 g/L | 0.218 | 0.663 | 0.7280 |
| Elovich model | | | |
| | $\alpha$ | $\beta$ | $R^2$ |
| 2.5 g/L | 0.321 | 5.302 | 0.7898 |
| 5.0 g/L | 0.421 | 2.876 | 0.8607 |
| 7.5 g/L | 0.484 | 1.925 | 0.8709 |
| 10.0 g/L | 0.633 | 1.416 | 0.8484 |

Notes: $k_{2,ad}$ is the rate constant of second-order biosorption (g/(mg h)). $q_{eq}$ is the amount of adsorbed at equilibrium time (mg/g). $k_d$ is the rate constants of intraparticle diffusion (mg/g $h^{1/2}$) and $C$ is a constants. $\alpha$ (mg/g h) and $\beta$ (g/mg) are the equilibrium rate constants for Elovich model.

### 3.3. Effect of initial phenol concentration

The results indicated that the variation in equilibrium sorption capacity of live *A. niger* for phenol depends on the initial phenol concentration (Fig. 4). As seen from Fig. 4, the biosorption capacity rose with increasing phenol concentration. When the initial phenol concentration was increased from 63 to 550 mg/L, the loading capacity of live biomass rose from 6.33 to 30.0 mg/g. The maximum loading capacity of the sorbent was also found to be 30.0 mg/g for live *A. niger* at an initial phenol concentration of 550 mg/L.

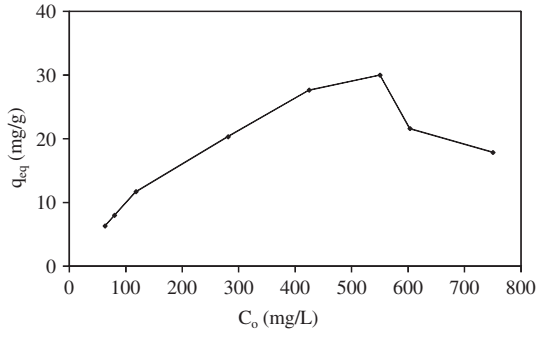


Fig. 4. The influence on the sorption capacity of initial phenol concentration (biomass concentration, 10 g/L; contact time, 48 h; agitating rate, 125 rpm; natural pH).

The rise in loading capacity of biomass with the increase in pollutant concentration may be due to higher probability of collision between phenol and biomass [2]. However, when phenol concentrations were raised above 550 mg/L it resulted in a reduction in biosorption capacity, which suggested a possible inhibitory effect of phenol on the biomass whose cell walls and/or other cellular components were used as chemical binding sites [7]. Thawornchaisit and Pakulanon [7] found that biosorption capacity rose when phenol concentration was increased from 4 to 110 mg/L at study that was performed with dried sewage sludge as a biosorbent for removing phenol from aqueous solution. However, phenol concentration above 110 mg/L resulted in a reduction of biosorption capacity. Previous studies by [20] as well as [21] did not observe the inhibitory effect of phenol on sorption capacity, instead they found that a saturation of cell-binding sites occurred when phenol concentration was greater than 500 mg/L [7]. This could be a plausible reason for the present study.

### 3.4. Equilibrium biosorption isotherms

The equilibrium data for the adsorption are commonly known as adsorption isotherms. Langmuir and Freundlich isotherms have been used to describe observed sorption phenomena of various phenol compounds on biosorbents. In this work, these two models were used to describe the relationship between the amount of phenol adsorbed and its equilibrium concentration in solutions at different phenol concentrations.

The Langmuir equation is valid for the monolayer adsorption. The sorption data of phenol have been correlated with Langmuir and Freundlich models, see Eqs. (2) and (3).

Langmuir isotherm is given by Eq. (2):

$$q_{eq} = \frac{Q^o \times b \times C_{eq}}{1 + b \times C_{eq}} \quad (2)$$

where $C_{eq}$ and $q_{eq}$ are the residual (equilibrium) pollutant concentration remaining in solution after binding (mg/L) and the amount of pollutant bound to the adsorbent (mg/g), respectively. $Q^o$ is the maximum amount of the pollutant per unit weight of the

adsorbent needed to form a complete monolayer on the surface bound at high $C_{eq}$ (mg/g), and $b$ is a constant related to the affinity of the binding sites (L/mg). $Q^o$ represents the practical limiting adsorption capacity when the surface is fully covered with pollutant molecules and assists in the comparison of adsorption performance, particularly in cases where the sorbent does not reach its full saturation in experiments. $Q^o$ and b can be determined from the linear plot of $C_{eq}/q_{eq}$ vs. $C_{eq}$ [20].

Freundlich isotherm is given by Eq. (3):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

where $C_e$ is the equilibrium concentration of the adsorbent (mg/L), $q_e$ is the amount adsorbed per unit mass of the adsorbent (mg/g), $K_F$ and $n$ are Freundlich constants with $n$ giving an indication of how favorable the adsorption process is. $K_F$ (mg/g (L/mg)$^{1/n}$) is the adsorption capacity of the adsorbent, which can be defined as the adsorption or distribution coefficient and represents the quantity of phenol adsorbed onto the adsorbent for a unit equilibrium concentration. The slope of $1/n$ ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value nears zero. A value below one for $1/n$ indicates a normal Langmuir isotherm, while a value above one indicates cooperative adsorption [22].

Equilibrium concentrations of the phenol compound were plotted to test their fit to the Freundlich and Langmuir equations (Figs. 5 and 6). The adsorption isotherms of the phenol compound, and the Freundlich and Langmuir constants evaluated from the isotherms and the correlation coefficients are given in Table 2.

It is seen from Table 2 that if isotherms are compared, the Langmuir isotherm would appear more suitable for the experimental data than the Freundlich isotherm because of its higher values of correlation coefficient.

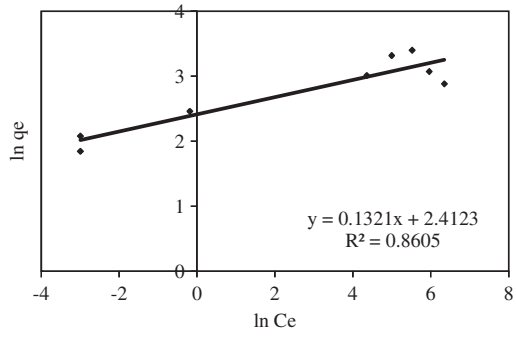


Fig. 5. Freundlich adsorption isotherms at different phenol concentration of the live *A. niger*.

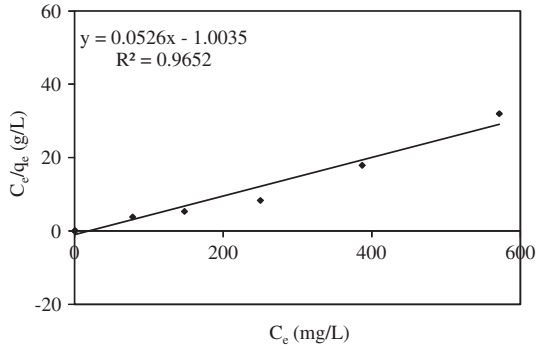


Fig. 6. Langmuir adsorption isotherms at different phenol concentration of the live *A. niger*.

Table 2
The parameters for Langmuir and Freundlich isotherms

| Isotherms | |
|---|---|
| Langmuir constants | |
| $Q^o$ (mg/g) | 19.011 |
| $b$ (L/mg) | 0.052 |
| $R^2$ | 0.965 |
| SSE | 8.14 |
| AIC | 6.54 |
| Freundlich constants | |
| $K_F$ (mg/g (L/mg)$^{1/n}$) | 11.160 |
| $n$ | 7.570 |
| $R^2$ | 0.861 |
| SSE | 17.03 |
| AIC | 12.45 |

Adsorption model constants, the values of which represent the surface properties and affinity of the sorbent, can be used to compare the sorptive capacities of different sorbents. As can be seen from Table 2, the values of $n$, when greater than one, indicate that the interaction between the phenol compound and live *A. niger* is strong and the phenol compound can be adsorbed greatly at the low concentration. Based on the data, we can hypothesize that the adsorption process involves the partition function as well as the chemical adsorption [17].

### 3.4.1. Comparison with AIC of adsorption isotherms

It is customary in batch adsorption studies to fit the equilibrium uptake data to several isotherms, then to use $R^2$ to compare the goodness-of-fit and select the

best isotherm model. With the best isotherm supposedly idendified, conclusions are usually presented regarding the homogeneity of the adsorbent surface and the mechanism of adsorption. Akaike's information criterion (AIC) [23] is a well-established statistical method that can be used to compare models. It is based on information theory and maximum likelihood theory, and as such, it determines which model is more likely to be correct and quantifies how much more likely. For a small sample size, AIC is calculated for each model from Eq. (4):

$$\mathrm{AIC} = N \ln\left(\frac{\mathrm{SSE}}{N}\right) + 2N_\mathrm{P} + \frac{2N_\mathrm{P}(N_\mathrm{P}+1)}{N - N_\mathrm{P} - 1} \quad (4)$$

where $N$ is the number of data points, $N_\mathrm{P}$ is the number of parameters in the model, and SSE is sum of the error squares.

The adsorption isotherms models having two parameters can be transformed into linear forms to obtain adjustable parameters just by graphical means or by linear regression analysis. But, the models having more than two adjustable parameters are not fitted to experimental data by linear regression or graphical means. In this case, it is necessary to apply non-linear least squares analysis. For that reasons, a minimization procedure has been adopted to solve isotherms and kinetic equations by minimizing the sum of error squared (SSE) between the predicted values and the experimental data using the solver add-in function of the Microsoft Excel. The term SSE generally refers to a "sum of squared errors."

The errors are the difference between the observed value and the value predicted by the model:

$$\mathrm{SSE} = \sqrt{\sum (q_\mathrm{exp} - q_\mathrm{cal})^2 / N} \quad (5)$$

where the subscripts "exp" and "cal" are the experimental and calculated values of $q$, espectively and $N$ is the number of measurements.

AIC values can be compared using the Evidence ratio which is defined by:

$$\text{Evidence ratio} = \frac{1}{e^{-0{,}5\Delta}} \quad (6)$$

where $\Delta$ is the absolute value of the difference in AIC between the two models [24].

The results of non-linear regression are presented in Table 2. This study concluded, on the basis of $R^2$ comparison, that the Langmuir isotherm is a better fit. However, AIC would be a more sound method to compare the goodness-of-fit to Langmuir and Freundlich isotherm. Accordingly, AIC values were calculated for Langmuir (6.54) and Freundlich (12.45) isotherms, respectively. Having a smaller AIC value suggests that Langmuir isotherm is more likely to be a better fit. The evidence ratio of 19.183 means that it is 19.183 times more likely to be the correct model than the Freundlich isotherm.

The parameters of each isotherm equation can be determined by minimizing the SSE. The best-fit model should have the least SSE value; therefore, this model can be obtained by comparing the SSE of each model. The SSE values are compared in Table 2. By comparing the SSE of different models in the two isotherm systems, it seems that Langmuir isotherm was the best fit.

### 3.5. Comparison with other adsorbents

The performance of different adsorbents for the removal of phenol has been demonstrated and varying values of the sorption capacity have been given in the literature. The maximum monolayer adsorption capacities of different adsorbents obtained from different sources are listed in Table 3, along with the values obtained in the present study. It can be stated that the uptake values determined in this study were found to be higher than that of many other biomasses. So, it can be seen that *A. niger* is a good and effective biomass that can be used for the removal of phenol as shown by the conditions of this study.

### 3.6. Effects of temperature on the removal of phenol

Temperature has a pronounced effect on the sorption capacity of the sorbents. Three temperatures, i.e. 298, 308, and 318 K, were selected for this study. The effect of temperature on the biosorption of phenol by live *A. niger* is shown in Fig. 7. As seen from Fig. 7, adsorption is affected by rising temperature. Thus, the optimum adsorption temperature at which the sorption capacity of phenol on biomass was the highest, was found to be 308 K in the temperature range studied. These results indicate that the biosorption of phenol by the live *A. niger* might be physical and endothermic in nature and the adsorption is favored at a higher temperature. If the adsorption process is controlled by the diffusion process (intra particle transport–pore diffusion) the endothermicity of the latter will cause the sorptive capacity to rise with increase in temperature.

In this study, sorption capacity decreased with rise in temperature from 308 to 318 K, while it increased

Table 3
Maximum adsorption capacities, $Q^o$ (mg/g), for the phenol compound by various adsorbents according to the Langmuir isotherm model

| Biomass or adsorbent | Operation conditions | | | | | Maximum biosorption capacity (mg/g) | Refs. |
|---|---|---|---|---|---|---|---|
| | $C_o$ (mg/L) | pH | $T$ (°C) | Biomass conc. (g/L) | Agitation rate (rpm) | | |
| Granular activated carbon | 100 | 1.0 | 25 | 0.5 | 125 | 268.4 | [25] |
| Dried activated sludge | | | | | | 236.8 | |
| Fly ash | | | | | | 92.5 | |
| *P. oceanica* fibers | 50 | 5.2 | 30 ± 2 | 0.01 | – | 5.2 | [26] |
| *Schizophyllum commune* fungus | 50–200 | 5.0 | 25 ± 2 | 4 | 220 | 120 | [27] |
| Granular activated carbon | 100 | 5.5 | 21 | 0.05–1 | 400 | 250 | [3] |
| Dried activated sludge | 100 | 1 | 25 | 0.5 | 125 | 236.8 | [2] |
| Chitosan–calcium alginate blended beads | 100 | 7 | Room temperature | 1 | 150 | 108.69 | [28] |
| İmmobilized activated sludge | 100 | 1.0 | 25 | 0.5 | 150 | 9.6 | [29] |
| *Sargassum muticum* | 200 | 1 | 20–25 | 2.5 | 175 | 4.6 ± 0.3 | [30] |
| Dried activated sludge | 25–300 | 6–8 | 25 | 1 | 150 | 52.35 | [31] |
| *Aspergillus niger* | 50–750 | 5–6 | 28 | 10 | 125 | 19.011 | This work |

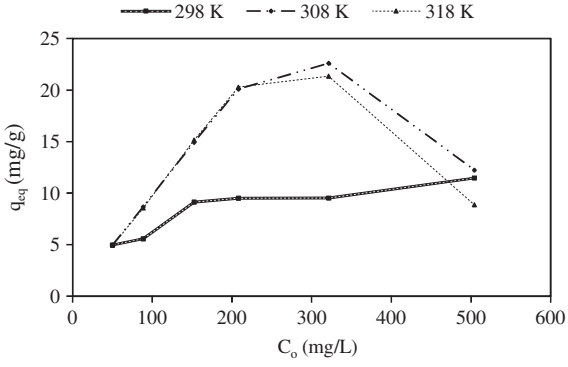


Fig. 7. Effect of temperature on biosorption capacity of *A. niger* (biomass concentration, 10 g/L; contact time, 48 h; agitating rate; 125 rpm; natural pH).

when temperature rose from 298 to 308 K. However, it suggested that the sorption process is endothermic since it was excess not decrease in the sorption capacity. Besides, temperature was not raised beyond 318 K since the formation of color was observed in the test solution.

The calculations of Langmuir and Freundlich isotherm constants at different temperatures and the corresponding coefficient of correlation values are shown in Table 4. The coefficients of the Langmuir model, $b$ lie between zero and one, suggesting that the adsorption of phenol on *A. niger* was favorable. Values of $Q^o$, which are defined as the maximum capacity of adsorbents, were also calculated from the Langmuir plots. With respect to the coefficients of the Freundlich model, $K_F$ increased with rise in the temperatures, revealing that the adsorption capacity of phenol onto *A. niger* increased with the rise in the temperature. Like $K_F$, $n$ increased with the rise in temperature. The highest value of $n$, 15.823 at 318 K represents favorable adsorption at high temperature. If the value of $n$ is below one, then the adsorption is a chemical process; otherwise, the adsorption is a physical process [32]. All values of $n$ exceed one, suggesting the adsorption of phenol onto *A. niger* is a physical process. As shown in Table 4, both the Freundlich and Langmuir models suggested that the adsorption capacity increased with the rise in the temperature, revealing that the adsorption was endothermic.

The correlation coefficients ($R^2$) of the Langmuir and Freundlich equation for the sorption of phenol on *A. niger* are also given in Table 4. Table 4 shows the Langmuir equation fits the sorption isotherms. The results of phenol sorption onto biomass were also analyzed using the Freundlich model to evaluate parameters associated with the sorption behavior. The Freundlich parameters for the sorption of phenol are

Table 4
Values of the Langmuir and Freundlich isotherm constants

| | Langmuir | | | Freundlich | | |
|---|---|---|---|---|---|---|
| $T$ (K) | $Q^o$ (mg/g) | $b$ (L/mg) | $R^2$ | $K_F$ (mg/g (L/mg)$^{1/n}$) | $n$ | $R^2$ |
| 298 | 11.628 | 0.046 | 0.9840 | 5.760 | 10.730 | 0.7148 |
| 308 | 12.300 | 0.137 | 0.9865 | 9.227 | 7.396 | 0.3942 |
| 318 | 8.953 | 0.097 | 0.9766 | 10.257 | 15.823 | 0.0943 |

also given in Table 4. The fit to the linear form of the models was verified by calculation of the correlation coefficient ($R^2$). $R^2$ values presented in Table 4 indicate that the adsorption data for the phenol removal fitted the Langmuir model better than the Freundlich model for all temperatures. Consequently, the sorption of phenol on the *A. niger* follows the Langmuir isotherm model, where the uptake occurs on the homogeneous surface by monolayer sorption without interaction between sorbent molecules.

### 3.7. Thermodynamic studies

A study of the temperature dependence of adsorption reactions gives valuable information on the enthalpy and entropy changes during adsorption. The standard Gibbs free energy change ($\Delta G^\circ$) is the fundamental criterion of spontaneity of a process and is determined using the equilibrium constant ($K_c$) by equation:

$$\Delta G^\circ = -RT \ln K_c \tag{7}$$

where $R$ is the universal gas constant (1.987 cal/K/mol or 8.314 J/mol/K) and $T$ is the temperature in Kelvin (K).

The equilibrium constant, $K_c$, can be calculated as

$$K_c = \frac{C_{ae}}{C_e} \tag{8}$$

where $C_{ae}$ and $C_e$ represent the equilibrium solute concentration on the adsorbent and in the solution, respectively. The standard enthalpy change ($\Delta H^\circ$) and standard entropy change ($\Delta S^\circ$) were obtained by applying the Van't Hoff equation that showed the dependence of equilibrium constant of the adsorption process on the temperature.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{9}$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{10}$$

when $\ln K_c$ is plotted against $1/T$, a straight line of slope $\Delta H^\circ/R$, and intercept $\Delta S^\circ/R$ is obtained. The values of $\Delta H^\circ$ and $\Delta S^\circ$ were calculated from the slope and intercept of the plot of $\ln K_c$ vs. $1/T$, shown in Fig. 8 (biomass dosage 10 g/L, contact time 48 h, pH 5 and 6) and the thermodynamic parameters ($\Delta G^\circ$, $\Delta H^\circ$, $\Delta S^\circ$) for the biosorption (298, 308, 318 K) and are noted in Table 5.

The standard Gibbs free energy change $\Delta G^\circ$ at all temperatures yielded a negative value, confirming that the adsorption of phenol onto *A. niger* was spontaneous and thermodynamically favorable. The greater the negative value of $\Delta G^\circ$ the stronger the driving force of adsorption reaction [33]. The values of $\Delta G^\circ$ were found to decrease as the temperature increased, indicating a lower driving force resulting in lower adsorption capacity [22]. The standard enthalpy change $\Delta H^\circ$ yielded a positive value, so the adsorption of phenol onto *A. niger* was an endothermic process. The positive adsorption standard entropy change $\Delta S^\circ$ may be interrelated with the affinity of the biomass for phenol and to the greater randomness at the

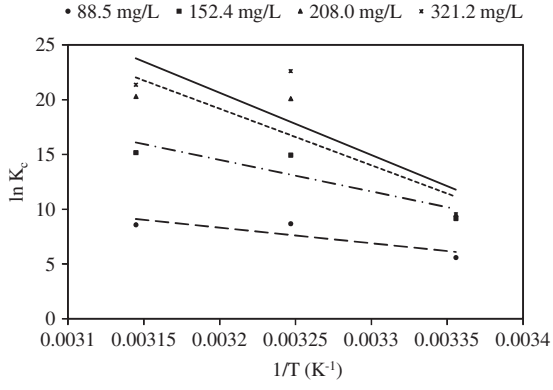


Fig. 8. Plot of $\ln K_c$ vs. $1/T$ for the estimation of thermodynamic parameters for biosorption of phenol onto *A. niger* biomass.

Table 5
Thermodynamic parameters for biosorption process

| $T$ (K) | $\Delta G^\circ$ (kJ/mol) | | | | |
|---|---|---|---|---|---|
| $C_o$ (mg/L) | 298 | 308 | 318 | $\Delta S^\circ$ (J/mol K) | $\Delta H^\circ$ (kJ/mol) |
| 88.5 | −13.850 | −22.228 | −22.686 | 450.33 | 119.11 |
| 152.4 | −22.671 | −38.259 | −40.110 | 886.82 | 239.45 |
| 208.0 | −23.588 | −51.473 | −53.673 | 1532.03 | 428.96 |
| 321.2 | −23.637 | −56.503 | −57.901 | 1681.86 | 471.99 |

solid–liquid interface during the sorption process [33]. Similar results have been demonstrated in the sorption of phenol on hydroxyapatite nanopowders [32].

## 4. Conclusions

Wastewaters containing phenolic compounds present a serious problem. Because of the presence of toxicity, wastewater containing phenols may not be released into the receiving waters without treatment. Recently, polymer-based adsorbents were widely employed for the removal of phenols. However, the high cost of polymers has stimulated pursuit of cheaper adsorbents. In this study, a cheaper raw material, *A. niger*, was used for the biosorption of phenol from aqueous solutions. The operating parameters, namely biomass dosage, initial phenol concentration, contact time, and temperature were found to influence the biosorption capacity of phenol. The present study indicates that *A. niger* can be used as efficient viable biosorbent for the removal of phenol from wastewaters. Sorption capacity rose when initial phenol concentration was increased up to 550 mg/L. However, it declined when the phenol concentration was higher than 550 mg/L. The maximum sorption capacity of *A. niger* was 30 mg/g for phenol. Besides, an inverse relationship between sorption capacity and amounts of biosorbent used was observed.

Adsorption isotherms of phenol compound on *A. niger* were studied and modeled using the Langmuir and Freundlich isotherm models. This study concluded, on the basis of $R^2$ comparison, that the Langmuir isotherm is a better fit. However, AIC would be a more sound method to compare the goodness-of-fit to Langmuir and Freundlich isotherm. Accordingly, AIC values were calculated for Langmuir (6.54) and Freundlich (12.45) isotherms, respectively. Having a smaller AIC value suggests that Langmuir isotherm is more likely to be a better fit.

Kinetic examination of the equilibrium data showed that the biosorption of phenol onto *A. niger* conformed closely to the intra particle diffusion model. The positive $\Delta H^\circ$ value confirmed the endothermic nature of the adsorption interaction, whereas the positive $\Delta S^\circ$ value showed the increased randomness at the solid solution interface during the adsorption process. The negative value of $\Delta G^\circ$ indicated it was feasible to use *A. niger* for adsorption of phenol and that this characteristic was of a spontaneous nature.

Based on all these findings, it can be concluded that *A. niger* is a biomass that is effective for the removal of phenol from aqueous solutions. Besides its considerable biosorption capacity, it is also an alternative that is naturally occurring renewable substance.

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