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Batch adsorption and desorption kinetic studies of bioactive phenolics on selected macroporous resins

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ABSTRACT

In this study, two different types of macroporous resins known as XAD-7HP and HP-20 were evaluated for the adsorption and desorption properties against bioactive phenolics extracted from Phanerochaete chrysosporium. The study was conducted at different phase contact time, solution pH and ethanol concentration by static adsorption and desorption methods. From the results, it was found that the adsorption capacity for both resins has no significant difference.Meanwhile in desorption study, HP-20 and XAD-7HP gave 90.52% and 88.28% recoveries, respectively. Then, the kinetic adsorption data were analyzed with both pseudo-first-order and pseudo-second-order equations and the later performed better. The adsorption isotherm data were fitted well by both Langmuir and Freundlich models.

1. Introduction

Phanerochaete chrysosporium is a filamentous basidiomycete white rot fungus that participates in the degradation process of complex woody materials. This fungus is the subject of many investigations due to its ability to mineralize lignin and other related molecules. It has great potential in many biotechnological applications including bioprotein production and bioremediation [1]. To the best our knowledge, there is no report of the production and recovery of bioactive phenolic compounds from the mycelia biomass of this basidiomycete. Owing to the increasing

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interest in new natural sources of antioxidant and antimicrobial compounds, this is the first study on Phanerochaete chrysosporium mycelia biomass as potential source of bioactive compounds. In this project, we propose to use Phanerochaete chrysosporium because our previous study showed the phenolic compounds extracted from this fungal biomass contained higher concentration of phenolics (300.58 GAE mg/l) and exhibited high scavenging activity (81.77%) against 2, 2-diphenyl-1-picrylhydrazyl (DPPH) as well as high antimicrobial activity againts Aspergillus niger,Bacillus subtilis and Escherichia coli [2]. Phenolic compounds promote benefits for human health and object of great interest of pharmaceutical and food industries [3]. However, crude phenolics extracted from plants and fungi are not suitable for direct applications as drugs and dietry supplements due to high level of impurities and low concentration of bioactive compounds.

A silica gel resin adsorption method is frequently used to concentrate and purify the phenolic compounds. However, this method suffers low recovery and low bioactivity due to degradation of the bioactive compounds. This method also causes excessive solvent wastage, safety problems and is not suitable for large-scale industrial production [4]. Otherwise, macroporous resins are durable non-polar and polar polymers having a high adsorption capacity with possible recovery of the adsorbed molecules, relative low cost, easy regeneration and improve bioactivity of the molecules [5]. At present, macroporous resins have been used widely for the separation and purification of many phenolic compunds including licorice flavonoids [6], scutellarin [7], chlorogenic acid [8], genistein and apigenin [9]. The advantages of macroporous resins have came to our interest to propose high quality and efficient chromatographic separation of bioactive phenolic compounds from crude extract of Phanerochaete chrysosporium biomass. This point out the necessity of systematic adsorption studies.

2. Experimentals

2.1 Chemicals and Reagents

The chemicals used were Folin-Ciocalteu Reagent, sodium carbonate, 95% ethanol, distilled water, sodium hydroxide (NaOH), hydrochloric acid (HCl).

2.2 Pretreatment of Macroporous Resins

The resins were pretreated by soaking in ethanol for 24 h. After removal of ethanol, the resins were washed by distilled water twice and subsequently soaked in 1 M NaOH for 5 h. Then, the resins were washed twice by distilled water. The washed resins were soaked in 1 M HCl for 5 h. Finally, the resins were washed by distilled water thoroughly. The pretreated resins were dried by an oven at 60 °C to constant weight [10].

2.3 Batch Adsorption Experiment

The extract obtained were undergone TPC and dissolved in 5 mL of distilled water to give a final concentration of 0.052 GAE mg.mL^{-1}. The pretreated resins were put into a 250 mL conical flask and the mycelial extract solution was added in each flask with initial pH of (pH=8.18). The weight of each resin (HP- 20 and XAD-7HP) used was (0.05, 0.1, 0.2, 0.3, 0.4 and 0.5g). The readings were taken every 30 minutes from each flask. These flasks were put into an incubator shaker at 25°C. Each flask were taken out according to the time set to determine of the concentration of the phenolics acids in the solution (supernatant) which were deducted with the initial concentration. Adsorption process completed due to reaching equilibrium, and was analyzed with the

spectrophotometer at 750 nm. The resins were separated from the solution using filter and were washed with 100 mL distilled water. The adsorption capacity was calculated using equation (1) and (2) [10];

Adsorption capacity:

$$q_e = \frac{(C_O - C_t)V_i}{W} \quad (1)$$

Adsorption capacity ratio:

$$A(\%) = \frac{(C_O - C_e)}{C_O} \times 100\% \quad (2)$$

2.4 Adsorption Kinetics

The kinetic data then were treated with two kinetics models which were in equations (3) and (4), respectively [10].

Pseudo-First-Order kinetics model:

$$lg(q_{e,1} - q_t) = lg(q_{e,1}) - k_1 \quad (3)$$

Pseudo-Second-Order kinetics model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e,2}^2} + \frac{t}{q_{e,2}} \quad (4)$$

where q_t and q_e are the adsorption capacity (mg/g dry resin), respectively. k_1 and k_2 refer to the rate constants of pseudo-first-order and pseudo-second-order kinetics models of adsorption process, respectively.

2.5 Adsorption Isotherms

The adsorption isotherm parameters were determined using equation (5) and (6), respectively [10].
Langmuir equation:

$$\frac{C_e}{q_e} = \frac{K_L}{q_m} + \frac{C_e}{q_m} \quad (5)$$

Freundlich equation:

$$ln(q_e) = \left(\frac{1}{n}\right) ln(C_e) + ln(K_F) \quad (6)$$

where, q_m is the maximum adsorption capacity to form monolayer (mg/g). K_L is the parameter referring to the affinity between resins and phenolics (ml/mg). However, K_F reflects the adsorption capacity of the resins and 1/n refers to the adsorption intensity of the resins.

2.6 Desorption Experiment

The 70 % of ethanol was used for the desorption process. The conical flasks were then placed on a shaker (150 rpm) at 25°C. The desorption capacity was calculated using equation (7).
Desorption capacity:

$$D(\%) = \frac{C_d V_d}{(C_o - C_e)V_i} \times 100\% \quad (7)$$

where, C_d, V_d and V_i are concentration of phenolics in desorption solution, volume of desorption solution and volume of initial sample solution, respectively.

2.7 Determination of Total Phenolic Content

The total phenolic content was determined according to the method suggested by Jamal *et al*. [11].

3. Results and Discussion

3.1 Adsorption and Desorption Capacities

Figure 1 shows the adsorption capacity curves of XAD-7HP and HP-20 resins at different pH values (5, 7 and 9). The adsorption capacity for both resins increased with the increasing of contact time and reached equilibrium within 200 min. The highest adsorption capacity was found at pH 7 for both types of resins. Therefore, the pH 7 of the extract solutions was set for the subsequent study. In desorption process, both resins have good desorption properties in the presence of 70% ethanol. The desorption ratio for XAD-7HP and HP-20 were 88.28% ± 3.14 and 90.52% ± 5.41, respectively.

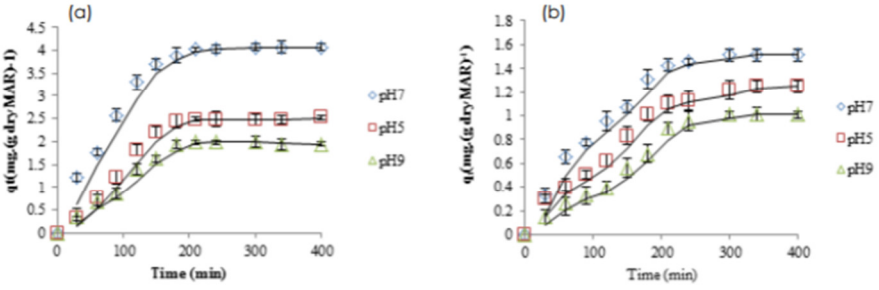

Fig. 1. Adsoprtion equilibrium curve for (a) XAD-7HP (b) HP-20

3.2 Adsorption Kinetics

Plotting $ln(q_e\text{-}q)$ against t for the pseudo-first-order equation and t/q_t against t for the pseudo-secondorder equation resulted in straight lines, respectively. Kinetics parameters were listed in Table 1. From linear regression analysis, it was found that the pseudo-second-order and the kinetics

equation describe the adsorption of phenolics onto the resins better. The adsorption process thus agreed with the assumption that bio-sorption follows a second order chemisorption [12]. The principle of the pseudo second-order assumed that the rate-limiting step for the adsorption process was the chemical adsorption. This can be explained in which the concentrations of both adsorbate and the adsorbent played the important role for the adsorption process. However, for the pseudo first-order of kinetic may only affect the early stage of the adsorption process as the model assumed that the adsorption rate is determined by the amount of the adsorption sites on the adsorbent surface [13].

Table 1
Kinetics parameters for the adsorption process by XAD-7HP and HP-20 at pH 7

Kinetics	**Type of adsorbent**	**Parameters**		**R^2**
		k_1	q_e	
Pseudo-first-order	XAD-7HP	0.016	5.75	0.9273
	HP-20	0.016	2.42	0.9144
Kinetics	**Type of adsorbent**	**Parameters**		**R^2**
		k_1	k_1	
Pseudo-second-order	XAD-7HP	0.00221	5.291	0.9726
	HP-20	0.00264	2.254	0.9359

3.3 Adsorption Isotherms

Adsorption isotherm shows the relationship of the adsorbate distribution between the liquid phase and the adsorbent when the adsorption process reaches the equilibrium phase. Data were plotted according to Langmuir isotherm and Freundlich isotherm and linearized experimental data obtained. All the data were plotted inside Table 2. Another characteristic of Langmuir equation can be calculated by using another equation of dimensionless constant R_L

$$R_L = \frac{1}{1+a_L C_o} \tag{8}$$

where a_L is a constant related to the affinity of the binding sites.

The value of R_L indicates the isotherm to be unfavorable where (R_L > 1), linear (R_L = 1), favorable (0 < R_L <1) and irreversible (R_L = 0) [14]. The R_L values calculated which were shown in Table 2 were found to be in the range of 0 and 1. Thus, showing that the adsorption process for both resins were favourable.

Table 2
Kinetics parameters for the adsorption process by XAD-7HP and HP-20 at pH 7

Type	**T(K)**	**Langmuir Equation**				**Freundlich Equation**			
		Q_o	***a_L***	***R_L***	***R^2***	***1/n***	***n***	***K_F***	***R^2***
XAD-7HP	298	15.748	15.875	0.394	0.8624	0.728	1.374	63.9755	0.9599
	308	16.785	11.037	0.4858	0.9068	0.7644	1.308	59.7817	0.9818
	318	10.7887	18.1765	0.3646	0.9127	0.608	1.645	31.5571	0.9810
HP-20	298	6.5232	35.6512	0.2263	0.982	0.5241	1.908	20.4299	0.9927
	308	8.826	16.9105	0.3814	0.9853	0.6834	1.463	31.9509	0.9921
	318	5.3107	36.2115	0.2236	0.9923	0.481	2.079	14.5399	0.9995

The plot of *Ln* C_e against *Ln* Q_e gave a straight line where the constant values of the Freundlich isotherm of K_F and *1/n* were calculated from the equation and presented in the Table 2. The constant values of the isotherm showed the relative adsorption capacity of the adsorbent and the intensity of the adsorption process. The value of *1/n* is a measure of the adsorption intensity on the surface or the surface heterogeneity. The value of the *1/n* cam indicates the isotherm shape of the process where $1/n > 1$ shows cooperative adsorption and $1/n < 1$ shows favorable adsorption. In this experiment, the value obtained showed in the range of 0 and 1, thus showing that the adsorption process for both resins were favourable. In this experiment, both of the resins showed more favored in the Freundlich equation as it gives higher R^2 compared to Langmuir isotherm. This describes that the resins works on monomolecular coverage layer of the adsorbent by the phenolics. It is usually used for an adsorption process on heterogeneous surfaces or surfaces that support sites of varying affinity [15] which differ from the Langmuir isotherm that supports the homogeneous surface.

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