Available online at www.derpharmachemica.com

ISSN 0975-413X
CODEN (USA): PCHHAX

Der Pharma Chemica, 2016, 8(6):96-103
(http://derpharmachemica.com/archive.html)

Biosorption of Phenol using dried Rice husk biomass: Kinetic and equilibrium studies

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ABSTRACT

Batch studies were conducted for kinetics and equilibrium studies on the biosorption of Phenol from aqueous solution by dried Rice husk biomass. The effect of pH, adsorbent dose, initial phenol concentration and contact time were investigated. Batch kinetic experiments showed that the adsorption followed pseudo-second-order kinetic model. The pH value of 3, contact time of 75 min, adsorbent dosage of 4 g/L and Phenol concentration 25 mg/L were determined as optimum conditions for adsorbents. The most Phenol removal efficiency was 99.1% in optimum conditions. The equilibrium adsorption data were analyzed using four widely applied isotherms: Langmuir, Freundlich, Doubinin–Radushkevich and Temkin. The results revealed that Langmuir isotherm fit the experimental results well. This study showed that dried Rice husk biomass could be used as an efficient sorbent for the removal of phenol from aqueous solution.

Keywords: Adsorption, Rice husk, Phenol, Isotherm, Kinetic model

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INTRODUCTION

Water pollution by organic chemicals is a major problem over decades. Owing to this, there is growing public concern over the contamination of groundwater by organic compounds[1, 2]. Phenol and its derivatives are considered as noxious pollutants, because they are toxic and harmful to living organisms even at low concentrations[3, 4]. Phenols are being discharged into the waters from various industrial processes such as oil refineries, petrochemical plants, ceramic plants, coal conversion processes and phenolic resin industries[5 ,6]. According to the recommendation of World Health Organization (WHO), the permissible concentration of phenolic contents in potable waters is 1 μgL^{-1} and the regulations by the Environmental Protection Agency (EPA), call for lowering phenol content in wastewaters less than 1 mg L^{-1} [7, 8]. By increasing the industrial wastewaters, the demand for removal of organic compounds including phenol has been increased[9]. Several methods, such as microbial degradation, adsorption, chemical oxidation, solvent extraction and reverse osmosis are being used for removing phenols from wastewater[10]. Adsorption is an effective separation process for treating industrial and domestic effluents[11]. Activated carbon is the most widely used adsorbent. It has the advantage of high adsorption capacity for organic compounds, but its use is usually limited due to its high cost[12]. Recently, considerable attention has been directed towards low cost, naturally occurring adsorbents[13]. In recent years agricultural wastes and by-products such as Sawdust[14], Canola[15] lemna minor[16], Azolla filiculides[17], cereal chaff[18] have been widely studied for the removal of pollutant from synthetic effluents. However, these low-cost adsorbents have generally low adsorption capacities and require large amounts of adsorbents[19]. Therefore, there is a growing need to find new, economical, easily available and effective adsorbents for practical application. Milling of rice crop produced rice husk as agriculture waste material having no commercial significance[20]. Approximately 80 million tons of rice husk are obtained annually[21]. The objective of this study is to investigate the capability of this lignocellulosic waste material, for the removal of phenol from aqueous solutions in batch system. The effects of different parameters like pH, biosorbent dose, initial Phenol concentration, contact time and temperature on the biosorption of phenol are studied. The equilibrium and kinetic data of biosorption studies are processed to understand the mechanism of phenol onto rice husk.

MATERIALS AND METHODS

Preparation of rice husk biomass: Rice husk was collected from the Sari city. It was boiled with distillate water and then filtrated and dried in oven at 80 ℃ for 24 h. Finally, It was sieved to particle size range of 1-2 mm. The crushed particles were then treated with 0.1M HCl for 5 h followed by washing with distilled water and then kept for shaded dry. The resultant biomass was subsequently used in sorption experiments[22].

The specific surface area of dried Rice husk was determined by the BET-N2 method using an ASAP 2000 apparatus based nitrogen adsorption–desorption isotherms at 77K. The surface images of dried Rice husk before and after adsorption process were captured by a Philips XL30 scanning electron microscope (SEM).

Adsorption experiments: All chemicals used in this work were of analytical reagent grade and were used without further purification. Deionized water was used for all dilutions. All glass ware and plastics were soaked in 10% (v/v) nitric acid solution for one day before use, and then cleaned repeatedly with deionized water. A stock solution of 1000 mg/L phenol was prepared by dissolving 1.00 g of phenol (Merck, Darmstadt, Germany) in 1 L of deionized water. The required concentration of phenol solutions were prepared by diluting the appropriate volumes of the stock solution. The pH of the solutions was adjusted to 7.0 by addition of 0.1 M HCl or 0.1 M NaOH solutions. The adsorption of phenol onto rice husk was investigated through a batch process. For adsorption experiments, 100 mL of phenol solution in the concentration range of 25–200 mg/L was transferred into a polyethylene centrifuge tube. Then 0.4 g of rice husk biomass (4 g/L suspension) was added to the solution, and then the mixture was agitated on a mechanical shaker (Edmund Bühler GmbH) at 180 rpm for 120 min. After reaching equilibrium, the suspension was filtered through 0.45 μm of nitrocellulose membrane and the filtrate was analyzed for residual phenol concentration using a double beam UV–vis spectrophotometer (DR 2800) at 500 nm by the 4-aminoantipyrene method. All experiments were conducted in triplicate, and the averages of the results were submitted for data analysis. The amount of the phenol adsorbed by the Rice husk biomass was calculated as following equation[23].

$$R = \frac{(C_0 - C_e)}{C_0} \times 100 \qquad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{M} \times 100 \qquad (2)$$

Co (mg/L) is the initial concentration of phenol solution, C_e (mg/L) is the equilibrium concentration of phenol in aqueous solution, V is the volume of the phenol solution (mL); and m is the weight of adsorbent (g).

Results and Discussion: Scanning electron microscopy (SEM) images were used to analyze the surface structure of Canola (Fig. 1). Fig. 1(a) clearly shows the pore textural structure of dried Rice husk before use. However, the Fig. 1(b) indicated that the clear pore textural structure is not observed on the surface of dried Rice husk after use which it could be due to either agglomeration on the surface or the invasion of phenol into the pores of dried Rice husk. The specific surface area of modified Rice husk was determined in the size of 51.5 m^2/g.

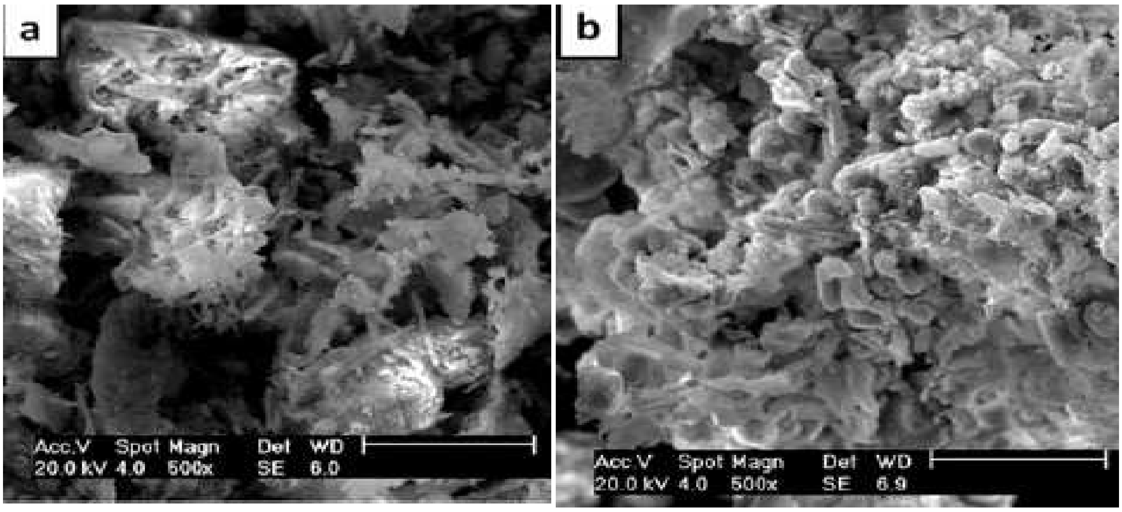

Fig.1: SEM image of Rice husk a:before used b: after used

Effect of Contact Time and Initial Concentration

The initial concentration gives an important driving force required to overcome all mass transfer resistances of all molecules between the aqueous and solid phases[24]. The effect of initial phenol concentration on adsorption as shown in Figure 2 was studied in the range of 25–200 mg/L of the initial phenol concentrations under the optimized conditions. Figures 2 showed rapid adsorption of phenol in the period and thereafter the adsorption rate declined gradually and reached the equilibrium at about 75 min. It was observed that, at the initial stage, adsorption rate is more, because of availability of more numbers of vacant sites[25]. After a certain period of time, the rate of adsorption decreases due to accumulation of adsorbate in the vacant sites[26]. It was also found from the figure 2 that the increase in initial phenol concentration enhances the interaction between phenol and active sites in biomass surface, thus decreasing the %removal of phenol with increase in concentration. Therefore, an increase in initial concentration of phenol decreased the adsorption uptake of phenol.

Effect of pH: It is well known that pH of the solution in one of the prime factors influencing the sorption's efficiency of the system[27]. The effect of pH on the adsorption characteristic of rice husk were determined in the pH 3 – 11, and constant other parameters (T =30 ℃ , Contact time 75 min and initial phenol concentration = 100 mg/L). The adsorption of phenol from aqueous solution is dependent on the pH of the solution which affects the surface charge o the adsorbent, degree of ionization and speciation of the adsorbate species[28]. The results are displayed in figure 3. As was expected, the adsorbed amount decreases with increasing the pH value. This can be explained on the basis that positively charged surface is formed on the adsorbents at a lower pH due to adsorption of hydrogen ions on the surface of adsorbents[29]. From the other hand at low pH, the concentration of H^+ ions increased and the surface of the biomass become positively charged[30]. A strong electrostatic interaction develops between positively charged biomass surface and negatively charged sites on the biosorbent[22].

Effect of adsorbent dosage

The effect of adsorbent dosage on the uptake of phenol by biomass was studied at different doses (0.05–0.8 mg/100 mL) for the concentration of 100 mg/L and the results were shown in Fig. 4. The removal of phenol was found to increase with an increase in adsorbent dosage. The removal of phenol remained almost constant at adsorbent dosage higher than 0.4 mg/L. This can be attributed to the increase in the adsorbent specific surface area and availability of more adsorption sites[31, 32].

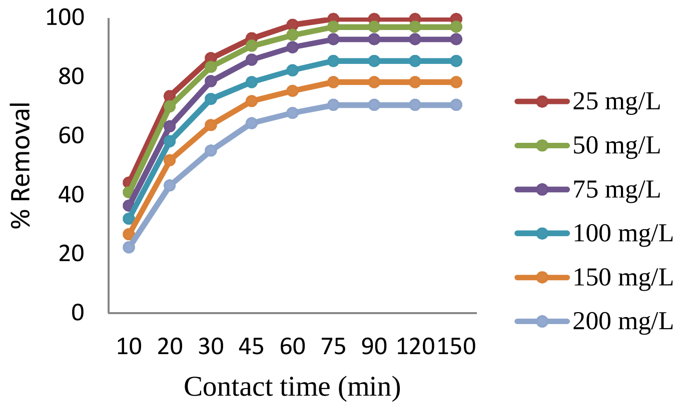

Fig.2. Effect of contact time and initial phenol concentration (pH = 7, dose 4 g/L , Temp: 30 °C)

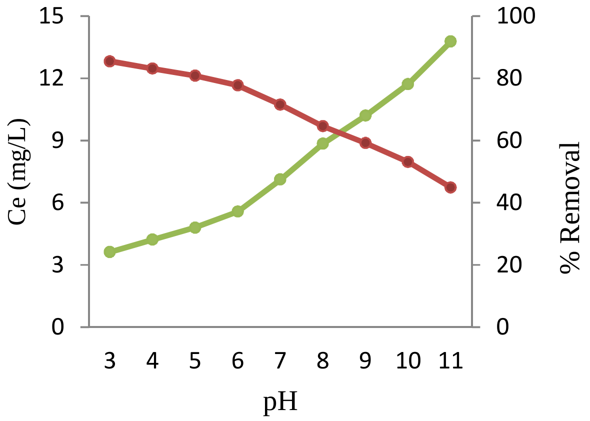

Fig.3. Effect of pH on phenol removal efficiency (C_0 = 100 mg/L, adsorbent dose of 4 g/L, contact time = 75 min)

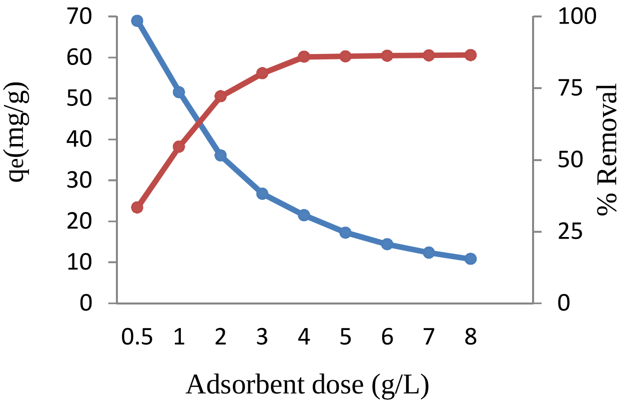

Fig.4. Effect of Adsorbent dose (C_0 = 100 mg/L, pH: 7, time: 75 min, Temp: 30℃)

Biosorption isotherms

Analysis of adsorption data is necessary for the development of biosorption isotherms, biosorption kinetics models. These models are used for optimization of design parameters.

The interaction between biosorbent and sorbate can be determined by the biosorption isotherm models. In this present study, six isotherms, named as the Langmuir, Freundlich, Temkin, Doubinin–Radushevich (D–R) isotherm models were investigated.

Langmuir isotherm: The Langmuir isotherm model suggests that the biosorption onto the adsorbent surface is homogeneous in nature. The linear Langmuir isotherm equation can be presented in the following equation[33, 34].

$$\frac{Ce}{qe} = \frac{1}{q_m K_L} + \frac{Ce}{q_m}$$

Freundlich Isotherm: The Freundlich isotherm model was chosen to estimate the adsorption intensity of the adsorbate on the adsorbent. Linear form of Freundlich model is expressed by[35, 36].

$$\text{Log } q_e = \frac{1}{n} \log Ce + \log K_F$$

K_F and 1/n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. 1/n values indicate the type of isotherm to be irreversible (1/n = 0), favorable (0< 1/n<1), unfavorable (1/n>1). The value of 1/n was less than one indicating the favorable adsorption.

Temkin Isotherm: Temkin isotherm suggests that the heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbate/adsorbent interactions. The linear form of Temkin isotherm is expressed as[37].

$$q_e = \beta \ln \alpha + \beta \ln C$$

where $\beta = (RT)/b$, T is the absolute temperature in K, R the universal gas constant, 8.314 J/molK, α the Temkin isotherm constant (L/g) and b is related to the heat of adsorption(J/mol).

Doubinin–Radushkevich (D–R) isotherm

Doubinin–Radushkevich model is a more generalized model as compared to the Langmuir isotherm. This model is based on the fact that there is no homogeneous surface or constant adsorption potential. The linear form of (D–R) isotherm model can be seen below[38].

$$\ln q_e = \ln q_m - K\varepsilon^2$$

Where K is a constant corresponding to the biosorption energy, q_m the theoretical saturation capacity and ε is the Polanyi potential which is calculated from equation below[39].

$$\varepsilon = RT \ln (1 + 1/C_e)$$

Where R ($kJ\ mol^{-1}\ K^{-1}$) is the gas constant and T (K) is the absolute temperature. E was calculated from the K value by the following relation[40].

$$E = 1/(2K)^{1/2}$$

The calculated values of isotherms parameters for the biosorption of phenol also given in table 1. The values of correlation coefficients for langmuir isotherms are high, so the langmuir model is fitted for phenol adsorption. The values of (E) that are shown in Table 1 indicates that the physico-sorption mechanism played an important role in the biosorption of phenol on the rice husk.

Table 1: Isotherm constants for phenol adsorption onto rice husk biomass

Isotherm models	2 g/L	4 g/L	Isotherm models	2 g/L	4 g/L
Langmuir			D–R		
q_m(mg/g)	37.25	21.95	q_m (mg/g)	29.11	16.44
K_L (L/mg)	0.032	0.065	K.10^4 (mol^2KJ^{-2})	6.14	4.32
R_L	0. 27	0. 49	E	0.34	0.61
R^2	0.997	0.999	R^2	0.812	0.839
Freundlich			Tempkin		
K_F (mg/g)	9.25	11.36	A (L/g)	0..278	0.451
n	2.76	3.31	B	27.36	31.45
R^2	0.961	0.945	R^2	0.845	0.865

Adsorption Kinetics: Kinetic studies are necessary to optimize different operation condition for the adsorption of phenol. The kinetics of phenol onto rice husk was analyzed using pseudo-first order kinetic, pseudo- second order kinetic and intraparticle diffusion models.

Pseudo First Order Kinetic Model: The model was suggested for the adsorption of solid/liquid systems. The integrated linear form of the model is as follows[41, 42].

$$\text{Log}\ (q_e - q_t) = \log q_e - \frac{K_1}{2.303}t$$

Where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium(mg/g), q_t is the amount of adsorbate adsorbed at contact time t (mg/g), k_1 is the pseudo-first order rate constant (min^{-1}). The values of the correlation coefficient obtained at all the studied concentrations are low, in the range 0.712–0.796. This suggests that the pseudo-first-order kinetic model is not suitable to describe the adsorption process.

The pseudo-second-order kinetic model can be expressed in linear form as follows[43, 44].

$$\frac{t}{q_t} = \frac{1}{k_2 . q^2} + \frac{t}{q_e}$$

where k_2 (g/mg min) is the rate constant of the pseudo second order. The parameters are listed in table 2. The values of the correlation coefficient are higher than 0.996 suggest that adsorption of phenol onto rice husk predominantly follows the pseudo-second-order kinetic model.

The intraparticle diffusion equation is written as follows[45, 46].

$$q_t = K\ t^{0.5} + C$$

Where C is the intercept which describes the foundry layer thickness and K (mg/g $min^{1/2}$) is the rate constant of intraparticle diffusion. According to results, values of coefficients of determination from table 2 are also low. From these results can conclude that the biosorption process of phenol onto rice husk biosorbent is not only depended on intraparticle diffusion but other mechanisms might be involved. Therefore, the data is not fitted well to the intraparticle diffusion model.

Table 2: kinetic parameters for phenol adsorption onto rice husk

Pseudo second-order model				Pseudo first-order model			Intraparticle diffusion		
C_o(mg/L)	k_2	R^2	q_e (mg/g)	K_1	R^2	q_e (mg/g)	K	C	R^2
25	0.029	0.998	4.25	0.124	0.712	2.89	2.48	1.76	0.794
50	0.054	0.996	10.73	0.235	0.764	7.93	3.97	2.98	0.806
100	0.072	0.994	25.19	0.411	0.745	16.45	5.15	3.72	0.832
200	0.093	0.997	44.66	0.659	0.796	38.14	7.86	2.19	0.859

CONCLUSION

The current study shows that rice husk can be used as an effective adsorbent for the removal of phenol from aqueous solution. It was found that the amount of phenol adsorbed depended on the parameters like contact time, adsorbent dosage, initial phenol concentration and pH. The adsorption capacity increases with increasing contact time and dose adsorbent. The equilibrium data have been analyzed using Langmuir, Freundlich, Temkin and D–R isotherms. The Langmuir isotherm was demonstrated to provide the best correlation for the adsorption of phenol onto rice husk. The kinetics of adsorption was studied by using pseudo-first order, pseudo- second order and intraparticle diffusion models. The results demonstrate that adsorption mechanisms in the system follow pseudo-second order kinetics.

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