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BIOSORPTION OF PHENOL BY A CHEMICALLY TREATED WILD MACROFUNGUS: EQUILIBRIUM AND KINETIC STUDY

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ABSTRACT

Phenol is one of the most common water pollutants found in industrial effluents. The phenol removal potential of a chemically modified macrofungus *Trametes sp.,* was investigated in a batch system. The effects of particle size, pH, temperature, contact time and biosorbent dosage have been investigated. The optimum conditions for phenol removal were found to be particle size: 150-300 µm, pH: 6.0 and biosorbent dosage: 6 g/L. The rate of biosorption of phenol was found to be rapid during the initial 30 min and equilibrium was established after 4 h. The results of equilibrium isotherm study showed that the data fitted well to Langmuir isotherm model within the concentration range studied (100-500 mg/L). The maximum adsorption capacity of the biosorbent was found to be 39.37 mg/g. Sorption kinetics was well described by pseudo-second-order kinetics. Desorption with 0.1 M NaOH resulted in 87% desorption of phenol from the biosorbent. The present study proved the applicability of *Trametes* sp., for the removal of phenol from waste waters.

KEYWORDS: ***Trametes sp.*, kinetics, phenol, Isotherm, Langmuir, Freundlich, desorption**

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INTRODUCTION

Phenolics are hazardous compounds because of their toxic characteristics. They are present in wastewaters of industries like pesticide, coke preparation, synthetic rubber, textile, colour, explosive, petrochemical etc. Phenol and phenolic compounds are among the most common toxic pollutants of wastewaters that require careful treatment before being discharged into the water bodies. When phenol containing water is chlorinated it can result in toxic polychlorinated phenols. While the Ministry of Environment and Forests, India has set a maximum concentration level of 1.0 mg/L of phenol in the industrial effluents for safe discharge into surface waters, the WHO recommends the permissible phenolic concentration of 0.001 mg/L in potable waters [1].Traditionally, chemical oxidation, solvent oxidation and adsorption onto activated carbon and other adsorbents are used for removal of phenols from wastewaters. These traditional treatment techniques, apart from causing damage to the environment, require enormous cost and continuous supply of chemicals as a result of which becomes impracticable and uneconomical. The search for an easy, effective, economical and eco-friendly technique for treatment of wastewaters has lead to the development of biological technologies in recent years. Biosorption is a biological phenomenon by which microorganisms like bacteria [2], fungi [3, 4], yeast [5] and algae [6] remove pollutants from aqueous environments. This term is used to indicate a number of metabolism-independent processes (physical and chemical adsorption, ion exchange, complexation, chelation and micro precipitation) taking place essentially in the cell wall [7]. The major advantages of biosorption are its cost effectiveness, high efficiency and reusability Both living and dead microbial biomass can be used to remove hazardous pollutants from wastewater, but maintenance of viable biomass during the biosorption process is cumbersome as it requires a continuous supply of nutrients and avoidance of toxicity. In contrast, the use of dead microbial biomass is advantageous for wastewater treatment in that dead organisms are unaffected by toxic wastes, they do not require nutrients and there is chance for regeneration and reusability.In the past decades studies on biosorption of phenol have been carried out using various live and dead fungal biomasses [8-11]. In this study, *Trametes* sp, a wild macrofungus was chemically treated and used as a biosorbent for the removal of phenol from aqueous solutions.*Trametes sp* a white-rot basidiomycete fungus is a potential bioremediation agent for a number of pollutants [12-15]. This macrofungus is inedible but recognized as a medicinal mushroom in Chinese medicine. It is commonly called as turkey tail and is a natural and readily available biosorbent and therefore, this biomass could be used as an economical tool for the removal of phenol from aqueous solutions. The objective of the present study was to investigate the biosorption potential of the chemically treated wild macrofungus *Trametes sp* in the biosorption of phenol. The influences of various parameters such as particle size, pH, contact time, biosorbent dosage and initial phenol concentration on biosorption of phenol has been studied. Equilibrium isotherm and kinetic studies have been carried out using different models and constants have been calculated under optimum conditions.

MATERIALS AND METHODS

Preparation and pretreatment of the biosorbent

Fruiting bodies of the white rot fungus *Trametes sp* were collected from tree trunks in an orchard washed thoroughly with sterile distilled water to remove the dirt particles and dried in an oven at 50°C for 48 h. The dried fruiting bodies were treated with 0.1 N sulphuric acid, washed with double distilled water and dried in an oven at 50°C for 48 h. The dried fruiting bodies were

pulverized in a hand grinder, sieved to desired particle size and used as biosorbent in batch.
All chemicals and reagents used in the experiments were of analytical grade. Phenol solutions of different concentrations were prepared by diluting 1000 mg/L of stock phenol solution, which was prepared by dissolving exact quantity of phenol in double distilled water. The pH of the solutions was adjusted to the required value using H_2SO_4 and NaOH solutions.

Biosorption studies in batch systems
Preliminary batch experiments were carried out to study the effect of particle size (150-300 µm, 300-450 µm and 450-600 µm) on biosorption of phenol. The effect of initial pH on biosorption of phenol was studied by varying the pH from 1 to 8. Erlenmayer flasks containing 100 mL phenol solution of known concentration and pH were agitated with 0.2 g of the biosorbent *Trametes sp* in a rotary shaker at 120 rpm. After the desired time period the biosorbent was separated from the phenol solution by filtration and the filtrate analyzed for residual phenol.

Sorption kinetic study
Sorption kinetic study was carried out using three different biosorbent dosages i.e., 2 g/L, 4 g/L and 6 g/L, with an initial phenol concentration of 100 g/L. The samples were withdrawn at different pre-decided time intervals. All these samples were filtered and analyzed for residual concentrations of phenol.

Equilibrium isotherm study
Isotherm studies were conducted with phenol solutions of different initial concentration ranging from 100 to 500 mg/L and a fixed biosorbent dosage. Equilibrium contact times determined from the kinetic studies aforementioned were used for these tests. After shaking for a certain period of time, the samples were filtered and analyzed for residual concentrations of phenol.

Desorption and regeneration of the biosorbent
Phenol solution of concentration 100 mg/L and a predetermined biosorbent dosage was agitated for an equilibrium contact time. After the equilibrium contact time the biosorbent was separated from the solutions and the residual phenol concentration was determined. The amount of phenol biosorbed onto the biosorbent was determined from the difference of initial and final concentrations of phenol in solution. The biosorbent was then dried overnight at 50°C and used for desorption studies. The phenol loaded biosorbent was agitated in a desorbing solution (0.1 M NaOH) for a desired period of time, filtered to regenerate the biosorbent and filtrate analyzed for desorbed phenol concentration. Distilled water was used as a control for desorption of phenol.The regenerated biosorbent was subjected to three consecutive cycles of biosorption followed by desorption alternatively.

Analytical methods
The residual phenol concentration in the biosorption medium was estimated spectrophotometrically (Hitachi U-2800). The absorbance of the coloured complex of phenol with p-nitroaniline measured at a wavelength of 470 nm [16].

RESULTS AND DISCUSSION

Effect of particle size
Experiments were conducted with biosorbent particles of different sizes of three ranges in order to determine the effect of particle size on sorption.

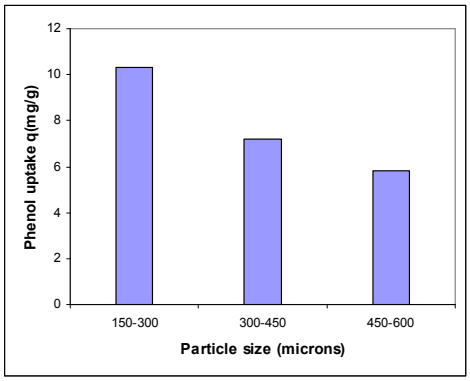

Figure 1
Effect of particle size on biosorption of phenol by chemically treated Trametes sp., (initial phenol concentration 100 mg/L, pH: unadjusted)

The sorption capacity for phenol increased with the decrease in the particle size as shown in Fig. 1. This is due to the fact that sorption being a surface phenomenon, smaller the sorbent particle size, comparatively larger surface area available for sorption of phenol [17].

Effect of pH

The initial pH of the biosorption medium is the most important single parameter influencing the sorption capacity. Effect of initial pH on biosorption of phenol was studied with an initial phenol concentration of 100 mg/L and a biosorbent dosage of 2 g/L. The experimental result for removal of phenol at different initial pH values is shown in figure 2. Maximum removal of phenol was observed at pH 6. The equilibrium phenol uptake was 15.8 mg/g. A significant decline in phenol uptake (q) was noticed for further increase in pH which may be attributed to the formation of phenolate ions.

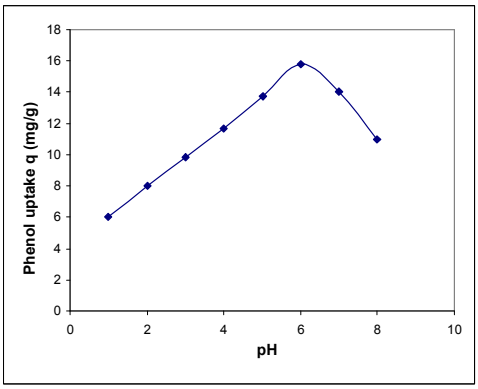

Figure 2
Effect of pH on biosorption of phenol by chemically treated Trametes sp., (initial phenol concentration: 100 mg/L, biosorbent dosage: 4 g/L, contact time: 6 h)

The pH of the biosorption solution leads to a change in the surface charge of the cells used as biosorbent. The surface charge of the fungal biomass is predominantly negative over a pH range of 3-10 [18, 19]. At pH value below 3.0 the overall surface charge of the fungal cells becomes positive. Pretreatment of the macrofungus with sulfuric acid would generate positively charged sites on its surface due to the binding of excess H^+ ions. Phenol has a pKa of

9.90 at 25°C and behaves as an anion at high pH values [20]. These observations indicate that at lower pH values (<6.0), acidic phenols are present and the neutral and undissociated phenolic compounds get preferably sorbed onto the surface of the biosorbent *Trametes sp*. The decrease in biosorption of phenol at higher pH (> 6.0) can be attributed to higher electrostatic repulsion when both the sorbent and sorbate are negatively charged [21]. Similar results were reported for biosorption of phenol by immobilized activated sludge [7].

Effect of contact time and sorption kinetics

Fig 3 shows the plot of phenol biosorption as a function of contact time at different biosorbent dosages 2 g/L, 4 g/L and 6 g/L.

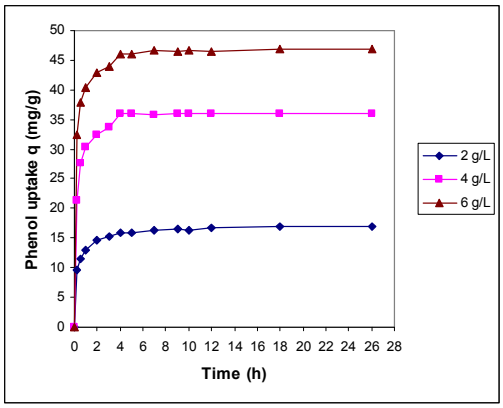

Figure 3
Phenol sorption kinetics at different biosorbent dosages (initial phenol concentration 100 mg/L, pH 6.0)

The rate of biosorption of phenol was found to be rapid during the initial 30 min of the experiment, while it gradually reduced until the attainment of equilibrium (4 h) because initially the adsorption sites are more available and phenol ions are easily adsorbed on these sites.This behavior has also been noticed for other toxic compounds and the existence of a two-step reaction model for toxic compounds sorption has already been reported [22, 23]. The first step is a rapid uptake phase in which the sorbate is sorbed in external surfaces and relatively large pores, while the second one is a slow phase where the sorbate slowly enters into small micropores due to the diffusion effect [24].The biosorption kinetics is one the most important parameter for designing sorption systems. In addition to the uptake capacity, the rate of uptake of the phenol by the biosorbent is also critical as far as the reactor configuration is concerned. A rapid kinetics will facilitate smaller reactors (lower retention time for effective uptake) whereas a slow rate of uptake will necessitate long column or series of columns to utilize maximum potential of the biosorbent. Sorption kinetics of phenol biosorption by chemically modified *Trametes* sp was analyzed using two simple kinetic models *viz*. the pseudo-first-order [25] and pseudo-second-order [26].

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

where q_t (mg /g) is the amount of substrate sorbed per specified amount of sorbent at time t (min), q_e is the amount sorbed per specified amount of sorbent at equilibrium time (mg/g), k_1 is the first order equilibrium rate constant (min^{-1}) and k_2 is the second order rate constant of sorption (g/mg/min). The linear plots for psudo-first-order and pseudo-second-order model are shown in figure 4 and 5. The correlation coefficients (R^2) for both the kinetic models were determined and compared. It was found that correlation coefficient for pseudo-first-order kinetic model was lesser than that of pseudo-second-order kinetic model (Table 1). Also, q_e(cal) values in the case of pseudo-second-order kinetic model were closer to the q_e(exp) values, which were obtained experimentally.

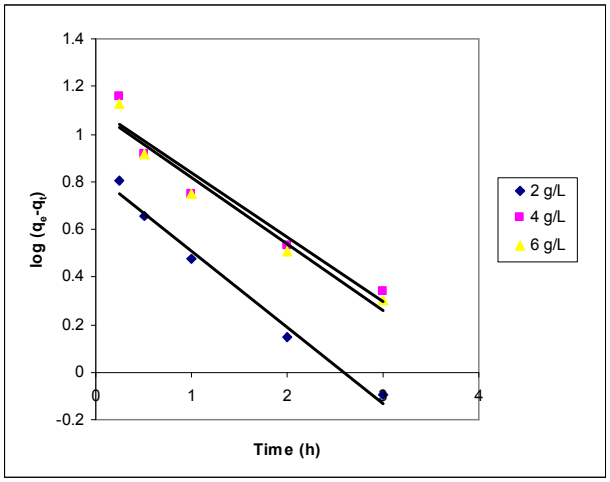

Figure 4
Pseudo-first-order kinetic model for biosorption of phenol by chemically treated Trametes sp.

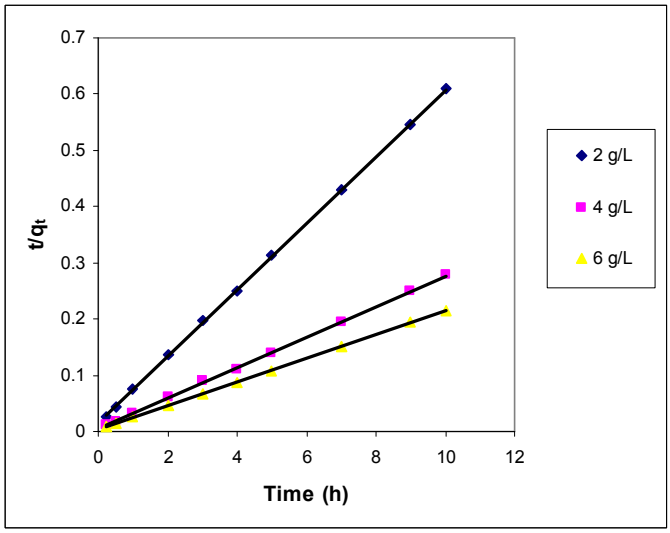

Figure 5
Pseudo-second-order kinetic model for biosorption of phenol by chemically treated Trametes sp.

These observations show that biosorption of phenol by *Trametes* sp followed the pseudo-second-order reaction, which suggests that the process controlling the rate may be a chemical sorption involving valence forces through sharing or exchanging of electrons between sorbent and sorbate [27].

Table 1
Kinetic model rate constants for phenol biosorption onto Trametes sp.

Biosorbent dosage (g/L)	q_e (exp) (mg/g)	First-order kinetic model			Second-order kinetic model		
		K_1 (min^{-1})	$q_{e,}$(cal) (mg/g)	R^2	K_2 (g/mg/min)	$q_{e,}$(cal) (mg/g)	R^2
2	16.0	0.7413	6.787	0.9862	0.2261	16.89	0.9998
4	35.9	0.6243	12.776	0.9300	0.1423	36.76	0.9997
6	46.0	0.6450	12.525	0.9529	0.1309	47.39	0.9999

Isotherm study

Experimental isotherm is useful for describing the sorption capacity of a specific biosorbent. Moreover, the isotherm plays a vital role for the analysis and design of adsorption systems as well as for model prediction. By plotting the solid phase concentration of phenol against the liquid phase concentration graphically, it is possible to depict the equilibrium biosorption isotherm. There are many theories relating to biosorption equilibrium. In the present investigation the equilibrium data were analyzed using Langmuir and Freundlich isotherm expression given by Eqs. (3) and (4), respectively [28, 29].

$$\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{C_e}{q_0} \qquad (3)$$

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \qquad (4)$$

where q_e is the equilibrium concentration of phenol on the biosorbent (mg/g), C_e is the equilibrium concentration of phenol in the solution (mg/L), q_0 is the monolayer biosorption capacity of the biosorbent (mg/g), b is Langmuir biosorption (L/mg) constant related with the free energy of biosorption, K_f and n are Freundlich constants relating the biosorption capacity and biosorption intensity respectively. Fig 6 and 7 shows the linear plot of Langmuir and Freundlich isotherms models respectively. The Langmuir constants q_0 and b were determined to be 39.37 mg/g and 0.0098 g/L respectively with a R^2 value of 0.9951. The K_f and n values obtained from the Freundlich isotherm were found to be 3.51 L/g and 2.70, respectively, with a R^2 value of 0.9411. From the R^2 values it is clear that the biosorption of phenol by chemically modified *Trametes sp* followed Langmuir isotherm model. The maximum biosorption capacities of different biosorbents reported in the literature are listed in Table 2 along with the values obtained in the present study.

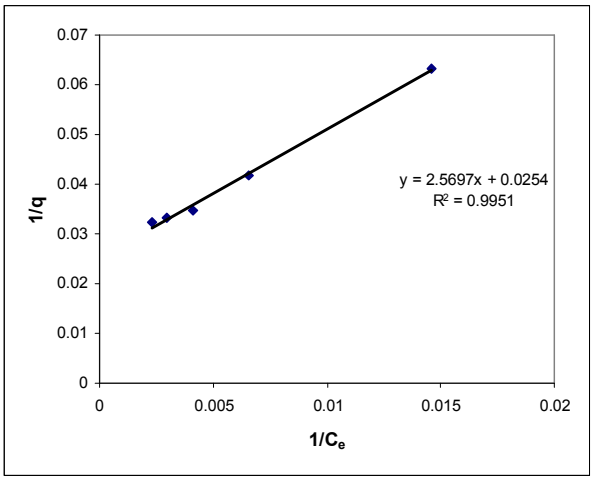

Figure 6
Langmuir isotherm plot for biosorption of phenol by chemically treated Trametes sp.

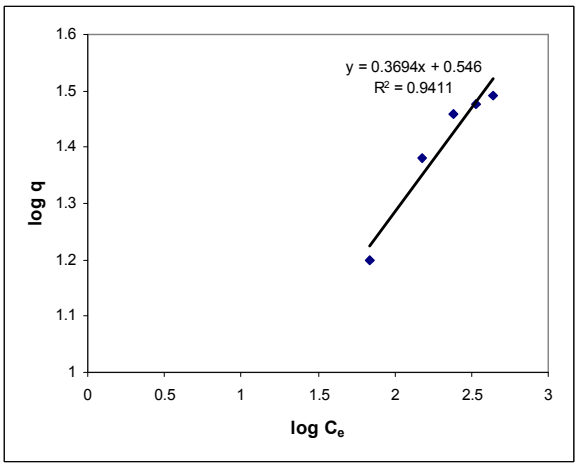

Figure 7
Freundlich isotherm plot for biosorption of phenol by chemically treated Trametes sp.

Table 2
Maximum biosorption capacities, q(mg/g), for the biosorption of phenol by various biosorbents

Biosorbent	**Phenol uptake capacity (q_0)(mg/g)**	**Reference**
Caulerpa scalpelliformis	*20*	*21*
S. muticum	*4.6*	*30*
Olive pomace	*11.40*	*31*
Rice husk	*4.5*	*32*
Chicken feathers	*19.5*	*33*
H2SO4-treated		
Aspergillus niger	*0.33*	*8*
Trametes sp.	*39.37*	Present study

Desorption and regeneration studies

Desorption with 0.1 M NaOH resulted in 87% desorption of the biosorbed phenol from the biosorbent *Trametes* sp. The control flask showed negligible concentration of phenol. The phenol uptake values (q) of the regenerated biosorbent in the three cycles of biosorption are shown in figure 8. Before regeneration, the metal uptake of the biosorbent was found to be 15.9 mg/g (data not shown in the above figure).

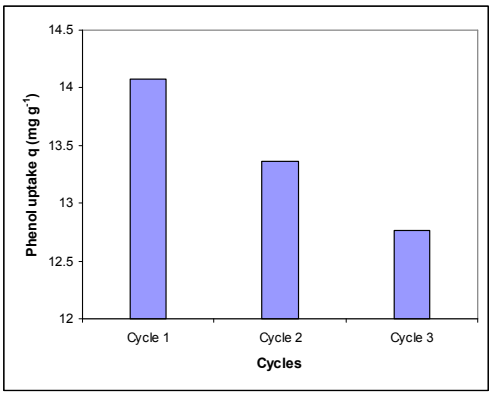

Figure 8
Biosorption of phenol in different cycles after regeneration with 0.1 N NaOH

It reduced by 12%, 16.5% and 20.2% respectively in the first, second and third cycle of biosorption after successive regeneration. This might be due to the unavailability of some of the binding sites which are still bound by the phenol ions that are not desorbed during the regeneration process.

CONCLUSIONS

The present study proved that chemically modified *Trametes* sp has considerable potential for removal of phenol from aqueous solutions over a wide range of concentrations. The uptake of phenol was influenced by particle size, initial pH, biosorbent dosage and contact time. Maximum removal of phenol was noticed with the smallest particle size used (150-300 µm) and at a pH of 6.0. The biosorption of phenol attained equilibrium after 4 h and the biosorption process followed pseudo-second-order kinetic model. Equilibrium biosorption data for phenol was analyzed by using Langmuir and Freundlich isotherm model and the isotherm constants were determined. It was found that the adsorption equilibrium data fitted very well to the Langmuir isotherm model. The biosorbent regenerated using 0.1 M NaOH was reused in three cycles of biosorption after successive regeneration. This study showed that the macrofungus *Trametes* sp could be used as an efficient biosorbent material for the removal of phenol from aqueous solution.

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