Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.807015

52 (2014) 1699–1704
February

Taylor & Francis
Taylor & Francis Group

Biosorption of phenol by dried biomass

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Received 5 December 2011; Accepted 13 May 2013

ABSTRACT

The adsorption of phenol onto dried biomass was studied as a function of initial phenol concentration, temperature, and particle sizes. The maximum phenol adsorption yields were obtained at the temperature of 30°C, the equilibrium uptake increased with increasing initial phenol concentration and the best adsorbed amounts were obtained for particle sizes between 0.05 and 0.40 mm for biomass Pleurotus Mutilus. The Freundlich and Langmuir adsorption models have been used for the mathematical description of the adsorption equilibrium. The results show that experimental data fit perfectly the Langmuir model.

Keywords: Adsorption; Phenol; Dried biomass; Pleurotus mutilis; Equilibrium

1. Introduction

Water pollution is a very persistent problem. In fact, the intensive discharge of different toxic substances without control constitutes a real danger for humanity. Each year we assist to the total or partial disappearance of many creations and plant species leading to an ecological disaster. Phenolic compounds are common contaminants in wastewater, generated by paint, pesticide, coal conversion, polymeric resin, petroleum, and petrochemical industries [1–4].

Phenols are generally considered to be one of the important organic pollutants discharged into the environment causing unpleasant taste and odor of drinking water [5,6]. Many of them have been classified as hazardous pollutants because of their potential to harm human health. Chronic toxic effects due to phenols reported in humans include vomiting, difficulty in swallowing, anorexia, liver and kidney damage, headache, fainting, and other mental disturbances. The maximum concentration of total phenols in drinking water is given as $0.5\,\mu g\,l^{-1}$ by the European Union [7,8]. Various techniques like coagulation, adsorption, chemical oxidation, reverse osmosis, ion exchange, solvent extraction, and froth floatation etc., have been used for the removal of phenol and related organic substances [5,9,3,10] from wastewaters. Among these techniques, adsorption is considered to be the most used due to its high efficiency and ability to separate a wide range of chemical compounds [5].

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Presented at the Third Maghreb Conference on Desalination and Water Treatment (CMTDE 2011) Hammamet, Tunisia, 18–22 December 2011

Many researchers [11–14] have shown that activated carbon is an effective adsorbent for organic compounds, especially for phenolic compounds, because it has a high surface area per unit mass and exhibits a high adsorption capacity for phenolic compounds. However, its high initial cost and the need for a costly regeneration system make it less economically viable as an adsorbent. Taking these criteria into consideration, the search for a low cost and easily available adsorbent has led many investigators to search more economic and efficient techniques using natural and vegetal adsorbents [6,15–18].

Several attempts were recorded in many laboratories in order to replace the activated carbon by other adsorbents such as dried biomass. Waste fungal biomass, which is a by-product of industrial fermentation, can be used as a cheap source of biosorbent. Amino, carboxyl, thiol, and phosphate groups present in the fungal cell wall are responsible for binding dye molecules [19]. Recent studies [20] have shown that different fungal biomasses (dead or alive), with or without any chemical or physical pretreatment, possess impressive adsorption capacities for heavy metal ions [21,22] and for color removal. Research works have been conducted to investigate removals of phenol and pentachlorophenol by pretreated fungal cells [23,24]. Earlier reports on biosorption of toxic organics with fungal biomass have indicated that better removals were obtained with dead fungal biomass than with live biomass [24] because there were no toxicity concerns, no requirements of growth media or nutrients and there were easy techniques to desorb contaminants from the biomass and reuse them.

The objective of this work is to study the static capacity of adsorption of phenol by dried biomass. The effects of initial phenol concentration, contact time, temperature, and granulometry on the static adsorption of the phenol on biomass have been examined. Finally, a modeling of the adsorption isotherms has been undertaken by fitting the parameters of the two traditional models: the Langmuir model and the Freundlich model.

2. Theory

The equilibrium study on adsorption has provided information on the capacity of the adsorbent. An adsorption isotherm is characterized by some constant values, which express the surface properties and affinity of the adsorbent. It can also be used to compare the adsorptive capacities of the adsorbent for different pollutants. This kind of adsorption isotherm generally fits the Langmuir and Freundlich models [25,26].

2.1. Langmuir model

The Langmuir model assumes the presence of a finite number of binding sites, homogeneously distributed over the adsorbent surface, presenting the same affinity for sorption of a single layer, and having no interaction between adsorbed species.

The well-known Langmuir expression [27] is presented as follows:

$$q_e = \frac{Q_0 k C_e}{1 + k C_e} \quad (1)$$

where q_e is the amount of phenol bound per gram of biomass at equilibrium (mg/g), C_e (mg/l) the residual phenol concentration in solution after binding, Q_0 (mg/g) the maximum amount of phenol per unit weight of biomass to form a complete monolayer on the surface bound at high C_e, and k (l/mg) a constant related to the affinity of the binding sites. A plot of $1/q_e$ vs. $1/C_e$ indicates a straight line of slope $1/kQ_0$ and an intercept $1/Q_0$.

2.2. Freundlich model

The Freundlich model as stated below is an empirical equation based on adsorption on a heterogeneous surface suggesting that binding sites are not equivalent and/or independent [28].

$$q_e = k_f C_e^{\frac{1}{n_f}} \quad (2)$$

where k_f and n_f are Freundlich parameters relating to the adsorption capacity and adsorption intensity, respectively.

From the linear plot of $\ln q_e$ vs. $\ln C_e$, k_f, and $1/n_f$ *values* can be determined.

3. Materials and methods

3.1. Preparation of Plurotus mutilus biomass

Pleurotus mutilus biomass is a result of industrial fermentation residue of an antibiotic (pleuromutilin) dedicated to veterinary use. This biomass is produced at the Antibiotic Complex of Médéa, Algeria (SAIDAL). It was used as adsorbents in dry form after several washes with distilled water and after chemical treatments with HCl. The biomass was oven dried at 105°C for 24 h, then crushed and sifted on a standard sifting and crushing.

3.2. Characterization of materials

The phenol concentration in the supernatant solution was analyzed using a UV spectrophotometer (SHIMADZU UV Mini-1,240) by monitoring the absorbance changes at a wavelength of maximum absorbance of 270 nm [5,6,29–31].

3.3. Preparation of adsorbate

A **s**tock solution was prepared by dissolving 0.5 g of phenol of analytical reagent grade in 500 ml of distilled water. The test solutions were prepared by diluting some stock solution up to the desired concentration. The range of phenol concentrations prepared from stock solution varied between 25 and 70 mg/l. The pH of each solution was adjusted to the required value pH = 6.5 with 1 N solutions of NaOH and H_2SO_4 after mixing with the biomass.

3.4. Process of adsorption

The method retained for the establishment of the adsorption isotherm consists in putting in a thermostated bath a series of bottles that were continuously stirred at 150 rpm. Each bottle contained a volume *(V)* of phenol solution of different known concentrations and a mass *(m)* of adsorbent (biomass). After a fixed contact time, the filtrate of the solution is recovered to be analyzed by UV/visible spectrophotometry.

The adsorbed quantity of aqueous solution per unit mass of the solid support *(q)* is calculated by the following formula:

$$q = (C_0 - C_e)\frac{V}{m} \quad (3)$$

where q is the adsorbed quantity of phenol per gram of adsorbent at time t (mg/g); q_e is the adsorbed quantity of phenol per gram of adsorbent at equilibrium (mg/g); C_e is the concentration of the solution at equilibrium (mg/l); C_0 is the initial phenol concentration (mg/l); V is the volume of phenol solution (l); m mass of biomass (g).

Thus, the curve of the isotherms adsorption is: $q\ (\text{mg}) = f(C_e\ (\text{mg/l}))$.

4. Results and discussion

Adsorption data for the uptake of phenol onto biomass were investigated at various initial concentrations, temperatures, and particle sizes. The results are given as the units of adsorbed phenol quantity per gram of adsorbent at time t (q, mg g^{-1}) and at equilibrium (q_e, mg g^{-1}), unadsorbed phenol concentration in solution at time t (C, mg l^{-1}) and at equilibrium (C_e, mg l^{-1}). Adsorption yield is given as:

$$\text{Adsorp. } \% = \frac{C_0 - C_e}{C_e} \times 100 \quad (4)$$

4.1. Effect of contact time

The variation of the quantity adsorbed according to the contact time is shown in Fig. 1. Adsorption studies were carried out for 2 h. It was observed that the amount of adsorbed phenol increased linearly with time at the beginning of adsorption. Then, saturation was reached at the equilibrium time. A larger amount of phenol was removed within the first 30 min of contact time, and the equilibrium was established in 50 min for the initial concentration 25 mg/l.

4.2. Effect of the initial concentration of phenol

The effect of initial phenol concentration was investigated in the range of 25–70 mg l^{-1} at 23 °C. The variation of the quantity adsorbed vs. the contact time at various initial phenol concentrations is shown in Fig. 1.

The sorption capacity of the sorbent was increased from 3.34 to 7.23 mg/g with increasing initial phenol concentration from 25 to 70 mg/l. The increase of loading capacity of Pleurotus mutilus biomass with increasing initial phenol concentration may also be due to higher interactions between phenol and Pleurotus mutilus biomass.

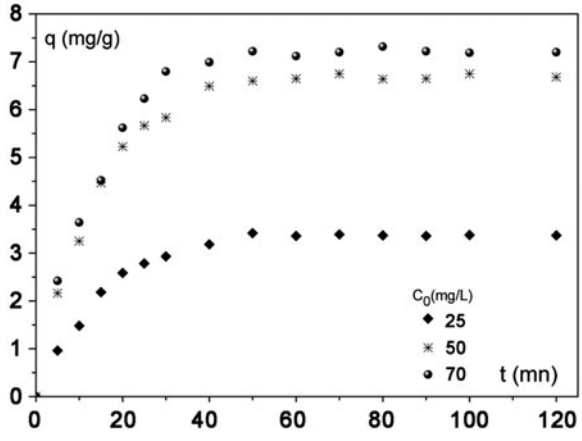

Fig. 1. The variation of adsorption capacity with adsorption time at various initial phenol concentrations at 23 °C, $V = 100$ ml, $m_s = 1$ g, $T = 23$ °C, stirring velocity = 500 rpm and $0.05 < d < 0.15$ mm.

4.3. Effect of the biomass granulometry

The tests were carried out for three kinds of biomass ($0.05 < d < 0.15$ mm), ($0.21 < d < 0.4$ mm), and ($d > 1$ mm). The influence of particle size was insignificant as shown in Fig. 2. Because dried biomass is too fine, there is no marked effect of particle size on the contact time required to reach equilibrium.

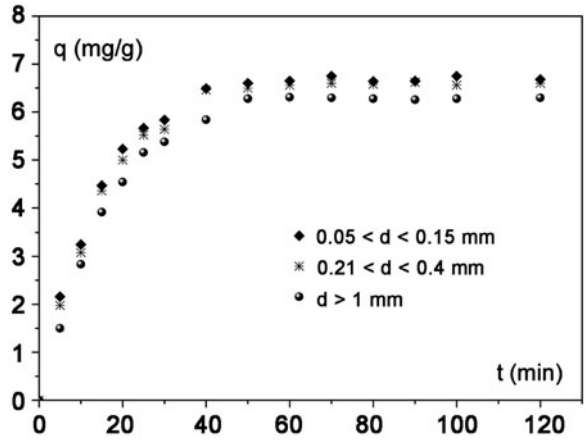

Fig. 2. Effect of variation of dried biomass particle size on the kinetics of phenol removal at 23℃.

4.4. Effect of phenol solution temperature

The yield of phenol removal from the solution increases from 68 to 84% by increasing the temperature of phenol solution from 23℃ to 30℃, respectively, as shown in Fig. 3. This indicates that the removal process was mainly accompanied by a chemical reaction which occurred between the phenol molecules and the dissolved portion of the biomass. By increasing the temperature from 30℃ to 45℃, the rate of phenol removal decreased as 84 to 56%, respectively. This result can be attributed to the changes in surface characteristics and activity of dried pleurotus mutilus biomass, which indicates the exothermic nature of the adsorption reaction. In this study, the highest sorption rate obtained was found to be 84% at a temperature of 30℃. At a higher temperature (> 30℃), the sorption rate was reduced.

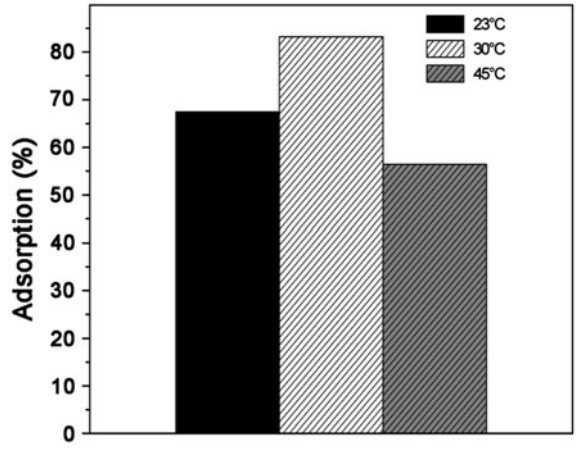

Fig. 3. Effect of solution temperature on the removal of phenol after 60 min.

4.5. Adsorption equilibrium depending on temperature

In this study, the adsorption equilibrium of phenol on dried biomass was modeled using Langmuir and Freundlich isotherms. The Langmuir and Freundlich adsorption constants evaluated from the isotherms are given in Table 1 with the correlation coefficients.

As seen from this table, although correlation coefficients of both equations are considerably very significant at all temperatures, the Langmuir model exhibited better fit to the adsorption data ($R^2 > 0.99$) than the Freundlich model. The maximum capacity, Q_0, determined from the Langmuir equation defines the total capacity of the adsorbent for phenol. The other Langmuir constant, k, indicates the affinity for the binding of phenol. The higher value of k found at 30℃ showed the strong bonding of phenol to the biomass at this temperature.

Table 1
Langmuir and Freundlich isotherm model constants and correlation coefficients for adsorption of phenol onto dried pleurotus mutilus biomass

T (℃)	Isotherm Langmuir model			Isotherm Freundlich model		
	Q_0 (mg/g)	k (l/mg)	R^2	K_f (mg/g(l/mg)$^{1/n}$)	$1/n_f$	R^2
25	7.6669	0.1882	0.9963	1.2301	0.5343	0.9500
30	5.3798	2.0638	0.9940	2.5273	0.3666	0.9734
45	4.9716	0.7329	0.9970	1.3402	0.3402	0.9640

Table 2
Comparison of adsorption capacity on various sorbents for phenol

Type of adsorbents	pH	Adsorption capacity (mg g^{-1})	References
Dried pleurotus mutilus biomass	6.5	7.66 (84% phenol removal)	Present study
Chitin	1	24.15	[34]
Loofa	6.5	6.21	[6]
Carbonized beet pulp	6.0	32.0	[5]
Activated coal		1.481	[35]
Activated carbon prepared from biomass material	6.5	149.25	[32]
Pseudomonas putida + activated sludge	7	80% phenol removal	[36]
Aspergillus niger	5.1	0.33	[23]
Caulerpa scalpelliformis	6	20.1	[37]
Dried sewage sludge	6.5	17.3	[38]
Phanerochaete chrysosporium	6.0	13.5	[33]
Ca-alginate beads (2%)	6.0	3.27	[33]
Immobilized *Phanerochaete chrysosporium*	6.0	7.81	[33]

Table 2 compares the adsorption capacity of different types of sorbents used for phenol adsorption. One may observe that low-cost material from activated carbon, prepared from biomass material, reported the highest adsorption capacity with 149.25 mg/g [32], whereas carbonized beet pulp [5] adsorption capacity was 32 mg/g. These results show that low-cost material can be employed as a promising adsorbent for phenol adsorption. Biosorption of phenol by phanerochaete chrysosporium, Ca–alginate beads (2%), and immobilized phanerochaete chrysosporium from aqueous suspensions was studied by Viktor Farkas and al [33]. The theoretical maximum adsorption capacities determined from the Langmuir model was 7.66 mg/g for the dried pleurotus mutilus biomass.

5. Conclusion

In this study, the batch adsorption of phenol on pleurotus mutilus biomass was investigated as a function of temperature, initial phenol concentration, and granulometry. The results showed that the solution temperature played an important role in the determination of the uptake capacities of sorbents. The optimum value of temperature was determined as 30˚C for pleurotus mutilus biomass. Adsorption increased as initial phenol concentration increased up to 50 mg/l. The results obtained for phenol-biomass system showed that the adsorption equilibrium data fitted the Langmuir model very well at all studied temperatures. In general, dried pleurotus mutilus biomass represents a remarkable affinity and potential for the removal of phenol from aqueous solutions at 30˚C. It may be concluded that dried pleurotus mutilus may be used as low cost and waste abundant sources for the adsorption of phenol as an alternative to activated carbon.

Symbols

C — unadsorbed phenol concentration in solution at any time (mg l^{-1})
C_e — unadsorbed phenol concentration in solution at equilibrium (mg l^{-1})
C_0 — initial phenol concentration (mg l^{-1})
k — adsorption equilibrium constant (l/mg)
k_f — Freundlich constant
n_f — Freundlich adsorption constant
m — mass of biomass (g)
q — adsorbed phenol quantity per gram of adsorbed at any time (mg/g)
q_e — adsorbed phenol quantity per gram of adsorbed at equilibrium (mg/g)
Q_0 — maximum amount of phenol per gram of biomass to form a complete monolayer on the surface (mg/g)
V — volume of the phenol solution (l)
R^2 — regression correlation coefficient
T — temperature (K, ˚C)

Acknowledgements

The authors are grateful to Pr Guillaume Polidori for his welcome at GRESPI (Groupe de Recherche En Sciences pour l'Ingénieur, Univ. Reims). We thank Dr Stephan Fohanno (GRESPI) for English language revision.

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