Journal of Environmental Management 90 (2009) 1877–1883

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Application of a chemically modified green macro alga as a biosorbent for phenol removal

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ARTICLE INFO

Article history:
Received 10 October 2007
Received in revised form
21 November 2008
Accepted 11 December 2008
Available online 11 January 2009

Keywords:
Phenol
Biosorption
Equilibrium isotherm
Green macro alga
Macro algae
Thermodynamic studies

ABSTRACT

Phenol and substituted phenols are toxic organic pollutants present in tannery waste streams. Environmental legislation defines the maximum discharge limit to be 5–50 ppm of total phenols in sewers. Thus the efforts to develop new efficient methods to remove phenolic compounds from wastewater are of primary concern. The present work aims at the use of a modified green macro alga (*Caulerpa scalpelliformis*) as a biosorbent for the removal of phenolic compounds from the post-tanning sectional stream. The effects of initial phenol concentration, contact time, temperature and initial pH of the solution on the biosorption potential of macro algal biomass have been investigated. Biosorption of phenol by modified green macro algae is best described by the Langmuir adsorption isotherm model. Biosorption kinetics of phenol onto modified green macro algal biomass were best described by a pseudo second order model. The maximum uptake capacity was found to be 20 mg of phenol per gram of green macro algae. A Boyd plot confirmed the external mass transfer as the slowest step involved in the biosorption process. The average effective diffusion coefficient was found to be 1.44×10^{-9} cm^2/s. Thermodynamic studies confirmed the biosorption process to be exothermic.

1. Introduction

Removal of phenol from industrial wastewaters is an important practical problem. Phenols and phenolic compounds are toxic to human beings, fish and to several biochemical fractions (Monteiro et al., 2000; Annadurai et al., 2002). It is among the list of priority organic pollutants proposed by the US Environmental Protection Agency (Yan et al., 2006). World Health Organization (WHO) prescribed 1 mg/L as the maximum permissible concentration of phenol in drinking water (Kumaran and Paruchuri, 1996). Hence, elimination of phenol becomes necessity to preserve the environmental quality. Different treatment methods are available for reduction of phenol content in wastewater, which include chlorination, ozonation, adsorption, solvent extraction, coagulation, flocculation and biological treatment (Klein and Lee, 1978).

Adsorption of phenol by activated carbon is the most widely used treatment method (Dabrowski et al., 2005). The main drawback is the capital intensiveness of activated carbon in wastewater treatment. The use of activated carbon also has several other drawbacks such as; regeneration of activated carbon, intraparticle resistance in adsorption process and high cost of manufacture. Hence, the use of low cost natural resources for the removal of phenol and phenolic compounds is being looked upon by the researchers in preference to other prevailing methods. Various adsorbents screened till date include wood, paper mill sludge, egg shell membranes, dried sewage sludge, aged refuse, chitin etc. (Tancredi et al., 2004; Calace et al., 2002; Koumanova et al., 2002; Thawornchaisit and Pakulanon, 2007; Xiaoli and Youcai, 2006; Dursun and Kalayci, 2005).

Green macro algae had been used as adsorbents for the removal of dyes (Aravindhan et al., 2007) and their efficiency toward the removal of heavy metals have also been demonstrated (Deng et al., 2007). Chelation and ion exchange play an important role in the adsorption mechanism in the heavy metal adsorption. Hydrophobic interaction seems to be responsible for the algae–phenol binding. In the case of biosorption of phenolic compounds, hydrophobic and donor acceptor interactions have been suggested as a driving force behind phenol biosorption processes.

Present work aims at the utilization of commonly available green macro alga *Caulerpa scalpelliformis* for the removal of phenol from aqueous solution. The effect of initial pH, temperature and adsorbent dosage on the phenol biosorption by the modified green macro algae has been investigated. The kinetics and the thermodynamics of biosorption have been studied. The equilibrium biosorption characteristics have been modeled using Langmuir and Freundlich isotherms.

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doi:10.1016/j.jenvman.2008.12.005

2. Materials and methods

Beach-dried green macro alga *C. scalpelliformis* was procured from Central Salt and Marine Chemicals Research Institute, Mandapam Camp, Ramnad District, India. The beach-dried macro algae were washed with distilled water, shade dried and stored in an airtight pack at room temperature 30 ± 1 °C. The moisture content of the dried macro alga was 5 ± 1% (w/w). The phenol used in this study was AR grade and of high purity, supplied by SRL (India). A commercial synthetic tanning agent (syntan) based on phenol condensate was employed as a model compound. All other chemicals and reagents used were of analytical grade.

2.1. Pretreatment of green macro alga

The air-dried macro algae were pre-treated with 0.1 N sulfuric acid before contacting them with the synthetic phenol containing solution. The pretreatment aids in stabilizing the algae and retain the reactive sites intact. The acid treated/protonated green macro alga was then washed with double distilled water. Finally, the washed materials were air-dried, crushed and sieved through 0.5 mm sieve. Crushed materials were then stored at room temperature in an airtight pack and used for further phenol removal experiments.

2.2. Characterization of the green macro algae

The FT–IR spectrum of the raw, modified and phenol treated green macro algae was obtained using the KBr disk technique. The macro alga was ground in a mortar for 5 min after drying it for a period of 2 h at 80 °C. Dilution and homogenization to 0.01% (w/w) with KBr (spectroscopic grade) were carried out with macro alga additional grinding. The disks were pressed in a hydraulic KBr press. The transmission FT–IR spectra were then recorded between 400 and 4000 cm^{-1} using a Perkin–Elmer Spectrum RX I FT–IR system. Surface area of the macro alga was measured using nitrogen adsorption–desorption isotherms recorded at −196 °C using Sorptomatic 1990 analyzer. Prior to analysis the samples were out gassed in the analyzer degas port for 2 h at 120 °C.

2.3. Preparation and analysis of phenol solutions

Stock solutions were prepared by dissolving 1 g of phenol and 1 g of synthetic tanning agent each in 1 L of double distilled water, respectively. The stock solutions were then suitably diluted and used for biosorption experiments. Two separate calibration graphs were obtained with the concentrations ranging from 0 to 120 mg/L for phenol and 0–70 mg/L for synthetic tanning agent, respectively. The concentration of phenol and the synthetic tanning agent was determined using a Perkin–Elmer Lambda 35 UV–vis Spectrophotometer at $\lambda_{max} = 270$ nm.

2.4. Biosorption experiments

The effect of initial pH of the solution on the amount of phenol adsorbed was obtained by agitating 6 g/L of protonated macro algal in a series of bottles, containing 50 mL of phenol solution of initial concentration 100 mg/L at different initial solution pH ranging from 2.0 to 10.0. (Increase or decrease in the pH of the solution, did not affect the optical density of the phenol solution). The agitation was provided for 6 h, which was well after the time of equilibration as observed from preliminary trials. The effect of the amount of macro alga used on the equilibrium uptake was estimated by agitating the phenol solution of initial concentration 100 mg/L with weighed amount of protonated macro alga ranging from 2 to 10 g/L. The effect of initial concentration on the equilibrium uptake was estimated by contacting 6 g/L of macro alga with 50 mL of phenol solution of different initial concentration ranging from 10 to 150 mg/L. Biosorption kinetics and equilibrium experiments were carried out by agitating 100 ml of phenol solution of known initial phenol concentrations with 6 g/L of macro alga. All the experiments were carried out at room temperature (30 ± 1 °C) with a constant agitation of 75 strokes/min on a thermostated water bath shaker. Samples pipetted out at different time intervals were filtered through a 0.45 μm pore size cellulose acetate membrane filter and then analyzed for the supernatant phenol concentration using Perkin–Elmer Lambda 35 UV–vis Spectrophotometer. The amount of phenol adsorbed on to the macro alga at equilibrium was calculated from the mass balance of the equation as given below:

$$q_e = (C_0 - C_e)\frac{V}{W} \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentration of phenol solution (mg/L), respectively, q_e is equilibrium phenol concentration on macro alga (mg/g), V is the volume of the phenol solution (L) and W is the mass of the macro alga used (g).

2.5. Experiments with commercial effluent

Post-tanning sectional wastewater from a commercial tannery, which employed the synthetic tanning agent used in this study, was utilized for the biosorption experiments. The amount of synthetic tanning agent present in the wastewater was expressed in terms of phenol. Phenol in the sectional wastewater was quantified with the help of a calibration graph. The optimal conditions as of phenol biosorption were employed for the treatment of the wastewater containing syntan. All the experiments were carried out in duplicate.

3. Results and discussion

It has been shown earlier that acid treatment of algal biomass leads to increase in the uptake of cations (Aravindhan et al., 2004; Volesky, 1990). Hence, in this study the air-dried green macro alga was treated with diluted sulfuric acid for a period of 30 min, washed well with distilled waster and air-dried. The single point surface area of the modified green macro algae was found to be 120 cm^2/g. The average pore diameter was observed to be 80 Å, proving to be a macro pore.

3.1. Effect of contact time

The biosorption of phenol onto modified green macro algae as a function of contact time at 30, 40, 50 and 60 °C is shown in Fig. 1. Biosorption studies were carried out for 6 h and it was observed that, the amount of adsorbed phenol increased linearly with time at the beginning of biosorption. A larger amount of phenol was removed in the initial 3 h of contact time and the equilibrium was established in 4 h at all temperatures studied.

3.2. Effect of initial pH

The most important parameter influencing the biosorption capacity is the pH of solution. The effect of initial pH on biosorption provides an insight on the nature of physicochemical interaction between solute in solution and the adsorptive sites of the adsorbent. Fig. 2 shows the effect of initial pH on the biosorption of phenol on to macro algae at given experimental conditions. Biosorption increases with increase in initial pH up to 6.0 and