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Short communication

Bioadsorption of pentachlorophenol (PCP) from aqueous solution by activated sludge biomass

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Abstract

The adsorption behavior of pentachlorophenol (PCP) from aqueous solution to activated sludge biomass was quantitatively characterized in this paper. The effects of the initial pH value and biomass concentration on bioadsorption were investigated. The Freundlich adsorption isotherm was applied to describe the biosorption processes and the isotherm constants were evaluated. The experimental results indicated that the initial pH value and biomass concentration are important parameters affecting the adsorption capacity that increased with decreasing biomass concentration (in the range less than 5 g/l) and pH (between 6 and 8). Both the biomass concentration and pH value only affected the capacity constant K_F of the Freundlich equation while the intensity constant n remained constant.

Keywords: Pentachlorophenol; Priority pollutant; Bioadsorption; Activated sludge

1. Introduction

Chlorinated phenolic compounds, which are generated from a number of industrial manufacturing processes, comprise the bulk of the environmental pollutants. Aqueous effluents from industrial operations such as polymeric resin production, oil refining, iron–steel, petroleum, pesticide, paint, solvent, pharmaceutics, wood preserving chemicals, coke-oven and paper and pulp industries contain chlorophenolic compounds. Their fate in the environment is of great importance as they are toxic, recalcitrant and bioaccumulating (Kishino and Kobayashi, 1994).

The conventional treatment technologies for removal of phenols and their derivatives from wastewater include biological treatment, the adsorption over activated carbon, air stripping, chemical oxidation, solvent extraction and incineration (Pellizzetti et al., 1990)

A variety of biological treatment processes, aerobic as well as anaerobic, such as facultative stabilization basin, aerated stabilization basin, aerated lagoon system, decanted aerated reactors, fluidized bed bioreactors, up-flow anaerobic sludge blanket (UASB) are employed to treat chlorophenolic wastewater. However, the efficacy of these treatment systems for the removal of chlorophenols is not good due to their toxicity and low biodegradability (Annachhatre and Gheewala, 1996).

Some chemical treatment methods such as ultraviolet light, ozone or hydrogen peroxide are capable of destroying chlorinated hydrocarbons in water, however, the high cost and low efficiency of these processes limit their applicability (Stephenson, 1992; White, 1992).

Adsorption is a well-established technique for treating domestic and industrial effluents. Use of activated carbon is a process based on the phase transfer from aqueous to solid phase. Activated carbon, in granular or powdered form, is the most widely used adsorbent. It has considerable capacity for the adsorption of organic molecules such as phenol. However, activated carbon is quite expensive and chemical and thermal regeneration of spent carbon is also expensive. Therefore, more economic, practical and efficient adsorbents are needed. Fly ash, peat, soil, rice husk and wood have been used for adsorption of organic pollutants (Binay and Narendra, 1994; Brasquet et al., 1996)

Bioadsorption is generally used for the treatment of heavy metal pollutants in wastewater. Application of bioadsorption for organic and other pollutants has

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received increasing attentions in recent years. Activated sludge is a biomass generated from wastewater treatment plant, which mainly consists of bacteria and protozoa. The cell wall of bacteria essentially contains various organic compounds, such as chitin, acidic polysaccharides, lipids, amino acids and other cellular components. The protozoa are unicellular, motile and relatively large eucaryotic cells that lack cell walls. They can adsorb components through their outer membranes which contain proteins and lipids (Schuler and Kargi, 1992).

It has been shown in recent studies that microbial cells tend to concentrate chemicals from their aquatic environment. The bioadsorption or accumulation of hazardous pollutants by microbial biomass bears a significant consequence as it might serve as the first step in introducing such toxic chemicals into the food chain. Furthermore, it has been shown that many toxic organic compounds that enter conventional biological wastewater treatment systems with the domestic and industrial wastes accumulate in the microbial sludge without substantial biodegradation occurring. The adsorption of hazardous organics by microbial sludge may complicate the management and the disposal of the waste sludge of municipal and industrial wastewater biological treatment plants as sludge may have accumulated hazardous organics that would be released back into the environment upon accumulation of sludge in landfills. On the other hand, there are ways in which this bioadsorption phenomenon could be considered beneficial. As hydrophobic organic pollutants show a high tendency to accumulate into microbial cells or sludge, the microbial biomass could be used as an adsorbent of biological origin for the removal of very low concentration hazardous organics from the wastewater.

The objective of this study was to characterize the adsorption behavior of pentachlorophenol (PCP) from waste streams to activated sludge biomass. The effect of initial pH value and biomass concentration on the sorption capacity were studied.

2. Methods

2.1. Adsorbent

Activated sludge was collected from a local biological wastewater treatment plant. The microbial biomass was centrifuged and then washed with distilled water and dried at 80°C.

2.2. Chemicals

Stock solutions were prepared by dissolving different amounts of analytical PCP in 0.01 M NaOH. The pH of the solution was adjusted to the required value by using a KH_2PO_4/Na_2HPO_4 buffer solution before mixing with adsorbent.

2.3. Bioadsorption experiments

Different amounts of activated sludge were added into each 10 ml of solution containing a known concentration of the organic pollutant in a 50 ml Erlenmeyer flask at the desired pH and temperature.

Flasks were agitated on a shaker at 125 revolutions per minute (rpm) and 25°C for 24 h, which should be more than sufficient time for adsorption equilibrium. Samples were taken at certain intervals, centrifuged and the supernatant used for analysis of PCP.

2.4. Analytical method

The PCP in samples was extracted with hexane. The concentrations of all samples in this work were determined with a gas chromatograph (Hewlett-Packard 5890A, HP, USA) using an electron capture detector.

3. Results and discussion

3.1. Adsorption equilibrium

In order to determine the time required for achieving sorption equilibrium, the sorption equilibrium experiments were performed at different initial concentrations of PCP. The results showed that the adsorption equilibrium was reached in less than 2 h under experimental conditions. No changes in PCP concentrations were observed during prolonged shaking. Therefore, a shaking time of 24 h, which should be long enough for achieving sorption equilibrium in the entire system was used in this study.

3.2. Adsorption isotherm analysis

The studies of isotherm of adsorption of PCP on to the activated sludge were conducted by varying the initial PCP concentrations from 25 to 500 μg/l, with adsorbent concentrations of 0.5 g/l, and a pH of 7.0. The results are illustrated in Fig. 1.

From Fig. 1, it can be seen that the equilibrium sorption capacity of the activated sludge for PCP increased with the increasing initial pollutant concentration. The increase of adsorption capacity of biomass with an increase in chlorophenol concentration may be due to a higher probability of contact between pollutant and activated sludge biomass.

The Freundlich model has been widely adopted to characterize the adsorption of organic pollutants from water and therefore was used in this work to fit the adsorption data. Attempts to use the Langmuir equa-

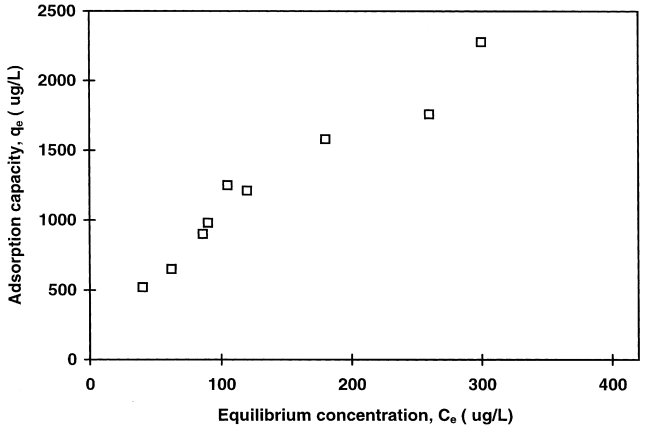

Fig. 1. The adsorption isotherm of PCP.

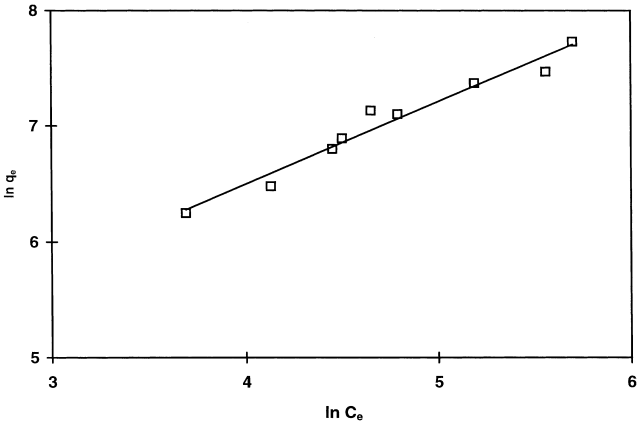

Fig. 2. Freundlich isotherm of PCP adsorption.

tion to fit the adsorption isotherm failed to provide a satisfactory correlation.

The Freundlich equation is used for heterogenous surface energies in which the energy term in the Langmuir equation varies as a function of the surface coverage strictly as a result of variation in the heat of sorption. The Freundlich equation has the general form

$$q_e = K_F c_e^{1/n}. \quad (1)$$

This equation can be also modified as

$$q_e = \frac{x}{M} = \frac{c_0 - c_e}{M} = K_F c_e^{1/n}, \quad (2)$$

i.e.,

$$M = \frac{c_0 - c_e}{x/M}, \quad (3)$$

where x is the amount sorbed; c_0 the initial concentration; c_e the equilibrium concentration of adsorbate and M is the amount of sorbent.

The sorbent dosage, M, required to reduce the initial concentration, c_0, so the desired final concentration, c_e, is calculated from Eq. (3). The value x/M at c_0 can be read from the plot of the Freundlich adsorption isotherm. This is helpful for large-scale applications of batch systems. A logarithmic plot linearizes the equation, enabling the exponent n and the constant K_F to be determined

$$\ln q_e = \ln K_F + \frac{1}{n} \ln c_e, \quad (4)$$

where q_e is the amount of sorbate per unit mass of sorbent; K_F the sorption capacity, indicator of sorption intensity and c_e is the equilibrium concentration.

The representative Freundlich isotherm for adsorption of PCP onto the activated sludge is shown in Fig. 2.

The values of constants K_F and $1/n$ have been calculated by the least-squares method and are shown in Table 1. K_F and $1/n$ give approximate measures of adsorbent capacity and intensity of adsorption, respectively.

Table 1
Effect of pH on isothermal constants of Freundlich model

pH	6.0	7.0	8.0
K_F	34.12	29.37	21.76
$1/n$	0.74	0.73	0.73
r^2	0.985	0.939	0.982

3.3. The effect of initial pH value

The effect of initial pH on the PCP adsorption was studied. The initial pH was adjusted to be 6, 7 and 8 with a KH_2PO_4/Na_2HPO_4 buffer solution. The experiments were carried out at 25°C and 125 rpm. The results are shown in Fig. 3.

It is apparent that the adsorption capacity decreased as the pH value was increased (Fig. 3). The equilibrium adsorption capacity dropped from 3040 to 2010 μg/l when the initial pH was increased from 6.0 to 8.0. The

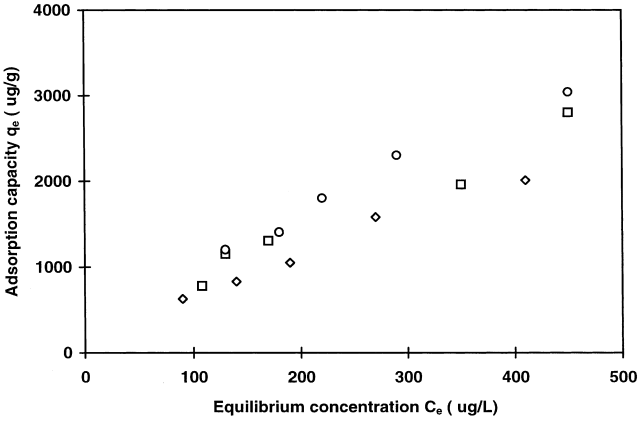

Fig. 3. The effect of initial pH on PCP bioadsorption: (○) pH 6.0; (□) pH 7.0; (◇) pH 8.0.

decrease in adsorption capacity of biomass with an increase in pH value may be due to the fact that as the pH increased, the overall surface charge on the cells became negative and this led to a lower electrostatic attraction between negatively charged PCP and binding sites of the biomass surface.

As shown in Fig. 3, the pH of the sorption medium is a key parameter that showed a substantial effect on bioadsorption capacity in the treatment of PCP.

The hydrogen ion concentration (pH) primarily affects the degree of ionization of the phenolic compound sorbate and the surface properties of the biomass sorbent. These in turn can lead to a shift in the sorption capacity of the equilibrium sorption process. It is a common observation that anions are favorably adsorbed on the surface of adsorbents at low pH because the presence of hydrogen ions renders the surface active for the adsorption of cations. In general, the adsorption rate of organic pollutants from aqueous solution increases with decreasing pH value. An explanation that appears more reasonable is that the increase in sorption observed at decreasing pH values may be caused by alterations in the sorbent surface, particularly its electrokinetic character, with changing hydrogen ion concentration. A decrease in pH probably results in a reduction of the negative charges at the surface of biomass (the isoelectric point of activated sludge would be usually between pH 1 and 3). As pH was lowered, the overall surface charge on the cells became positive and this led to electrostatic attraction between negatively charged phenolic compound and positively charged binding sites. As the pH increased, however, the overall surface charge on the cells became negative and bioadsorption decreased.

The isothermal data were linearilzed using the Freundlich equation (Fig. 4) and the regression constants are tabulated in Table 1.

As shown in Table 1, the Freundlich parameter K_F, an indicator of sorption capacity, decreased with an increase in pH value, whereas, the other Freundlich parameter, n, which indicates sorption intensity, remained constant.

The high value of correlation coefficient indicated that the data conformed well to the Freundlich model and a strong relationship existed between the parameters.

3.4. Effect of biomass concentration

The effect of activated sludge concentration on the adsorption of PCP was investigated. The biomass concentration varied from 0.5 to 5.0 g/l. The pH was maintained at 7.0. The results are shown in Fig. 5. The data were also linearized using the Freundlich model (Fig. 6) and the regression constants are listed in Table 2.

The effect of biomass concentration demonstrated quite interesting dependencies. On the one hand, as was expected, the percentage of the PCP removal increased

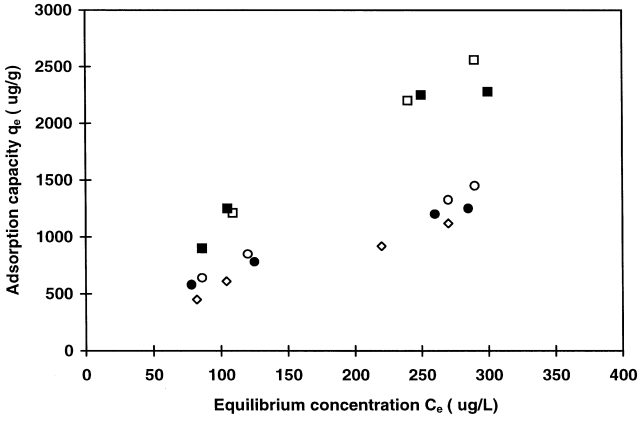

Fig. 5. The effect of biomass concentration on PCP bioadsorption: (□) 0.5; (■) 1.0; (○) 2.0; (●) 4.0; (◇) 5.0 g/l.

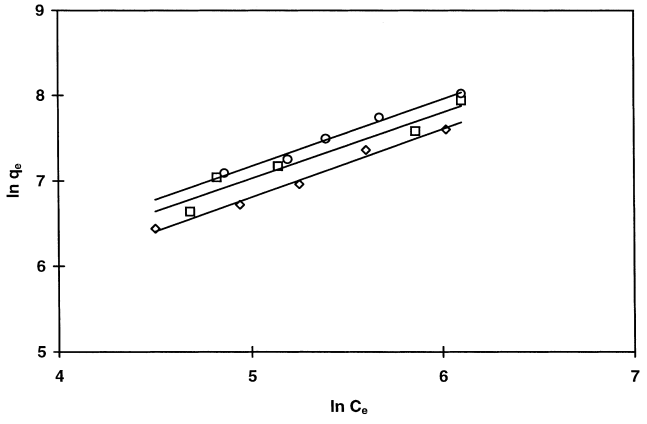

Fig. 4. Freundlich isotherm for PCP bioadsorption under various pH values: (○) pH 6.0; (□) pH 7.0; (◇) pH 8.0.

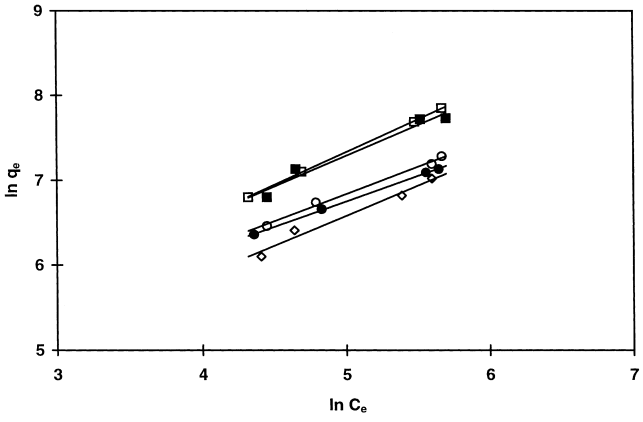

Fig. 6. Freundlich isotherm for PCP bioadsorption under various biomass concentrations: (□) 0.5; (■) 1.0; (○) 2.0; (●) 4.0; (◇) 5.0 g/l.

Table 2
Effect of biomass concentration on isothermal constants of Freundlich model

Biomass (g/l)	0.5	1.0	2.0	4.0	5.0
K_F	30.78	26.63	19.64	17.05	14.50
$1/n$	0.781	0.795	0.764	0.770	0.781
r^2	0.995	0.968	0.980	0.944	0.983

with the increasing activated sludge amount (data not shown). But conversely, the absorbed amount of PCP per biomass quantity decreased with the increasing biomass concentration (Fig. 5). The adsorption capacity dropped from 2560 to 1120 μg/l when the biomass concentration was increased from 0.5 to 5.0 g/l. The drop in adsorption capacity was due to binding sites of the biomass remaining unsaturated during the adsorption reaction.

Tsezos and Bell (1989) reported on the sorption of PCP to living and dead biomass. Two types of biomass were used, a mixed culture of aerobic activated sludge and a pure culture of *Rhizopus arrhizus*. Based on their results it appears that bioadsorption can be described by the Freundlich equation. The bioadsorption process involves both adsorption by the cell walls and uptake by other cellular components of the microbial biomass. They also found that it was impossible to generalize on the relative magnitude of bioadsorption uptake between live and nonviable biomass. Brandt et al. (1997) investigated the adsorption and desorption of PCP on cells of *Mycobacterium chlorophenolicium* PCP-1. They found that in contrast to the results of Tsezos and Bell (1989), PCP is only adsorbed on the cell wall and sorption equilibrium was normally reached in less than 1.5 min.

4. Conclusion

The adsorption isotherm of PCP on to the activated sludge can be described by the Freundlich equation. Based on the results it appears that both pH value and biomass concentration were important parameters. However, they appear to affect only the capacity constant K_F, while the intensity constant, n, remained constant.

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