TSINGHUA SCIENCE AND TECHNOLOGY
ISSN 1007-0214 02/17 pp241-245
Volume 5, Number 3, September 2000

Bioadsorption of 4-Chlorophenol to the Activated Sludge

WANG Jianlong (王建龙), Nigel Horan†, Ed. Stentiford†, QIAN Yi (钱 易)

State Key Joint Laboratory of Environment Simulation and Pollution Control,
Department of Environmental Science and Engineering,
Tsinghua University, Beijing 100084, China;
† School of Civil Engineering, Leeds University, LS2 9JT, UK

Abstract The adsorption behaviour of 4-chlorophenol from aqueous solution to activated sludge was quantitatively characterized in this paper. The effects of the initial pH values, initial chlorophenol concentration and adsorbent dosage on bioadsorption were investigated. The maximum adsorption capacity was found to be 110.5mg/g at 100mg/L initial concentration. The Freundlich and Langmuir adsorption isotherms were applied to describe the biosorption processes and the isotherm constants were evaluated.

Key words 4-chlorophenol; priority pollutant; bioadsorption; activated sludge

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[1].

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[2].

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, upflow 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[3].

Some chemical treatment methods such as ultraviolet light, ozone, or peroxide are capable of destroying chlorinated hydrocarbons in water, however, the high cost and low efficiency of these processes limit their applicability[4,5].

The destruction of organic compounds by incineration faces considerable social pressure, which applies a rigid control in order to avoid or minimize the generation and emission of other hazardous compounds such as dioxins.

Adsorption is a well-established and powerful technique for treating domestic and industrial effluents. Use of activated carbon is 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 a good capacity for the adsorption of organic molecules, such as phenol. However, activated carbon is quite expensive and the both chemical and thermal regeneration of spent carbon is also expensive. Therefore, more economic, practical and efficient adsorbents are needed. So far, fly ash, peat, soil, rice husk and wood have been used for adsorption of organic pollutants[6-11].

Bioadsorption is generally used for the

Received: 1999-08-15; revised: 1999-12-08

treatment of heavy metal pollutants in wastewater. Application of bioadsorption for the removal of organic and other pollutants from aqueous solution has received increasing attention in recent years. Activated sludge is a biomass generated from wastewater treatment plants, 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, relatively large eucaryotic cells that lack cell walls. They can adsorb components through their outer membrane which contain proteins and lipids[12].

Recent studies have shown 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. 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. As hydrophobic organic pollutants show a high tendency to accumulate into microbial cells or sludge, the microbial biomass could be used as a biological origin adsorbent for the removal of very low concentration hazardous organics from the wastewater.

The objective of this study is to investigate the adsorption of chlorophenol by activated sludge from aqueous solution, to optimize the adsorption conditions and quantitatively describe the adsorption behaviour.

1 Materials and Methods

1.1 Adsorbent

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

1.2 Chemicals

Stock solution was prepared by dissolving 1.0 g of chlorophenol of analytical reagent grade in 1 L of distilled water. The ranges of concentration of chlorophenol prepared from stock solution varied between 25 and 500 mg/L. The pH of the solution was adjusted to the required value with 2 mol/L HCl before mixing with adsorbent.

1.3 Analytical method

4-chlorophenol concentrations were determined spectrophotometrically. The absorbance of the colored complex of 4-chlorophenol with 4-aminoantipyrine was read at 510 nm.

1.4 Bioadsorption

Different amount of activated sludge were added into each 100 mL of solution containing a known concentrations of organic pollutant in a 250 mL Erlenmayer flask at the desired pH and temperature.

Flasks were shaken on a rotary shaker at 125 r/min and 25℃ for 10 h. Samples were taken at a certain intervals and centrifuged, then the supernatant was used for analysis of chlorophenol.

2 Results and Discussion

2.1 Bioadsorption characteristics

0.5 g of dried activated sludge was added into 100 mL of chlorophenol solution (100 mg/L). The experiments were carried out at 25℃ and 125 r/min in a constant temperature shaker bath for 5 h in order to determine the effect of time on bioadsorption. The results are shown in Fig. 1.

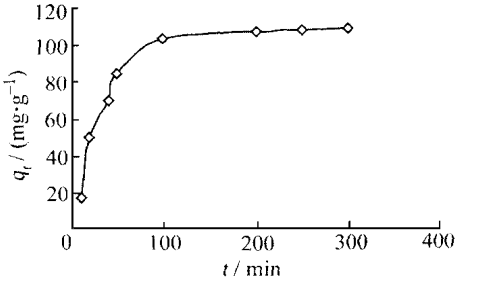

Fig. 1 Effect of time on bioadsorption of chlorophenol on activated sludge

Figure 1 showed that the adsorption process reached equilibrium state at about 300 min and q was about 110.5 mg/g. The adsorption performed very quickly at the beginning, more than 60% of the adsorption capacity achieved at 30 min, which indicated that the external mass transfer resistance is small, chlorophenol can easily reach the active sites on the surface of microbial biomass.

2.2 Effect of initial pH value

The effect of initial pH on the adsorption was studied. The initial pH was adjusted to be 1, 2, 4, 6, 8, 10, the experiments were carried out at 25℃ and 125 r/min. The results are shown in

Fig. 2.

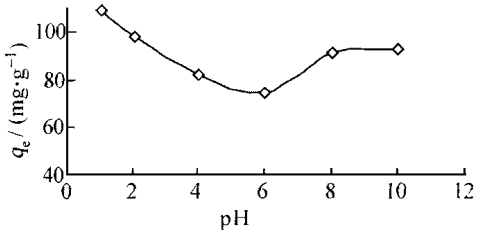

Fig. 2 The effect of initial pH on 4-chlorophenol bioadsorption

As shown in Fig. 2, the pH of the sorption medium is a key parameter that affects bioadsorption capacity in the treatment of chlorophenol. pH primarily affects the degree of ionization of the chlorophenol and the surface properties of the biosorbent, i. e., surface charge of the cells. Figure 2 clearly showed that as the pH was lowered, the overall surface charge on the cells became positive and this led to electrostatic attraction between negatively charged phenols and positively charged binding sites. As the pH increased, however, the overall surface charge on the cells became negative and bioadsorption decreased. The optimum pH value for chlorophenol adsorption on to activated sludge was around 1. 0.

2. 3 Effect of initial chlorophenol concentration

The initial chlorophenol concentrations varied from 25 to 500 mg /L, the adsorbent concentration was 0. 5 g /L, the pH was 1. 0. The results are illustrated in Fig. 3.

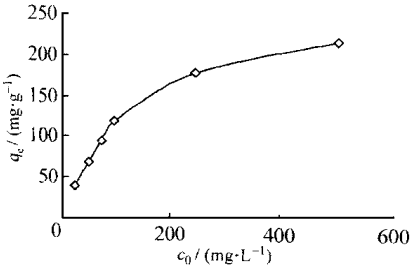

Fig. 3 The effect of initial 4-chlorophenol concentration on adsorption capacity

From Fig. 3, we can see that the equilibrium sorption capacity of the activated sludge for 4-chlorophenol increased with the increase of initial pollutant concentration up to 500 mg /L. When the initial adsorbate concentration increased from 25 to 500 mg /L, the equilibrium adsorption capacity increased from 40 to 220 mg /g. The increase in adsorption capacity of biomass with the increase of chlorophenol concentration maybe caused by higher probability of collision between pollutant and the activated sludge biomass.

2. 4 Effect of the biomass dosage

The effect of activated sludge amount demonstrated quite interesting dependencies. On one hand, as was to be expected, the percentage of the chlorophenol removal increases with the increasing activated sludge amount (Fig. 4).

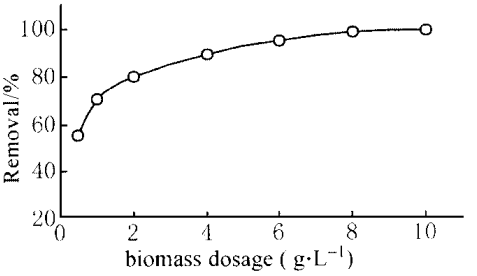

Fig. 4 The effect of biomass dosage on removal of chlorophenol

But, the sorbed amount of pollutant on the per unit quantity biomass decreases with the increasing biomass amount (Fig. 5).

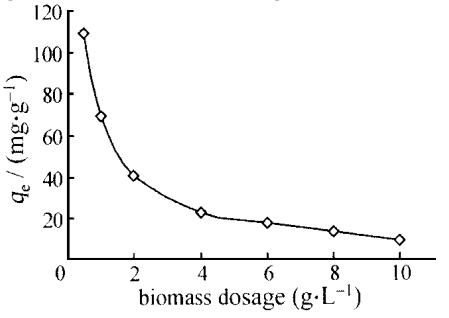

Fig. 5 The dependence of q_e on the biomass amount

The adsorption capacity dropped from 110. 4 mg /g to 9. 98 mg /g by increasing the adsorbent dosage from 0. 5 g /L to 10 g /L. The drop in adsorption capacity is basically due to those sites which remained unsaturated during the adsorption reaction.

2. 5 Bioadsorption kinetics

Several steps can be used to express the mechanism of solute adsorption to an adsorbent. In order to investigate the mechanism of adsorption, the rate constant of chlorophenol bioadsorption to activated sludge was determined using Lagergren equation, a pseudo-first order model.

The adsorption kinetics may be described by a pseudo-first order, the diffusion equation is

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

Integrating equation (1) for the boundary

conditions $t=0$ to $t=t$ and $q_t=0$ to $q_t=q_t$, gives:

$$\ln\left(\frac{q_e}{q_e-q_t}\right)=k_1 t \quad (2)$$

where, q_e is the amount of chlorophenol adsorbed at equilibrium, mg/g; q_t is the amount of chlorophenol adsorbed at time t, mg/g; k_1 is the equilibrium rate constant of pseudo-first adsorption, min^{-1}.

Equation (2) can be rearranged to obtain a linear form:

$$\ln(q_e-q_t)=\ln q_e-k_1 t \quad (3)$$

In order to obtain the rate constants, the straight-line plot of $\ln(q_e-q_t)$ against t has been analyzed (Fig. 6). The rate constant k_1 and correlation coefficients r^2 were calculated from this plot, they are 2.07×10^{-2} min^{-1} and 0.96, respectively.

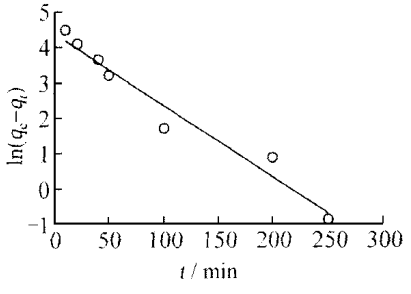

Fig. 6 The plot of $\ln(q_e-q_t)$ against t

2.6 Isotherm analysis

The equilibrium of adsorption is one of important physicochemical aspects for the evaluation of the adsorption process. The isotherm of adsorption of chlorophenol onto the activated sludge was studied and the results were shown in Fig. 7.

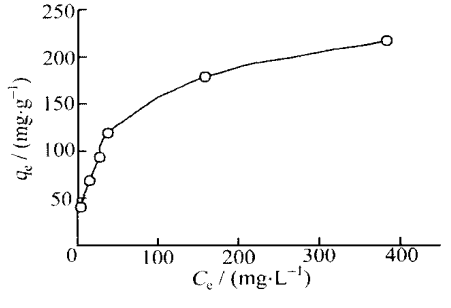

Fig. 7 Adsorption isotherm of chlorophenol to activate sludge

In order to model the sorption behaviour, Langmuir and Freundlich models are used to fit the adsorption data. The Langmuir isotherm is valid for monolayer sorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of sorption onto the surface and no transmigration of sorbate in the plane of the surface. The Langmuir equation is given as:

$$\frac{c_e}{q_e}=\frac{1}{bX_{max}}+\frac{c_e}{X_{max}} \quad (4)$$

where, c_e is the equilibrium concentration of sorbate, mg/L; q_e is the adsorption capacity at equilibrium, mg/g; X_{max} is the maximum adsorption capacity, mg/g; b is the Langmuir constant, mg^{-1}.

The linear plot of c_e/q_e versus c_e confirm the validity of the Langmuir model for this process (Fig. 8). The constants were calculated and given in Table 1.

Table 1 Isotherm constants of adsorption of chlorophenol

Langmuir constants			Freundlich constants		
X_{max} (mg/g)	b (mg^{-1})	r^2	K_F (mg/g)	n^{-1}	r^2
237.3	0.027	0.996	24.78	0.384	0.967

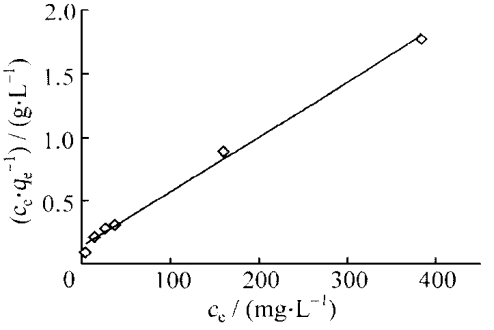

Fig. 8 Langmuir isotherm of chlorophenol adsorption

The Freundlich equation is used for heterogeneous 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:

$$q_e=K_F c_e^{1/n} \quad (5)$$

A logarithmic plot linearizes the equation, enabling the exponent n and the constant K_F to be determined:

$$\ln q_e=\ln K_F+\frac{1}{n}\ln c_e \quad (6)$$

where, q_e is the amount of sorbate per unit mass of sorbent, mg/g; K_F is sorption capacity, indicator of sorption capacity, mg/g; n is Freundlich constant, indicating sorption intensity, mg^{-1}; c_e is the equilibrium concentration, mg/L.

The representative Freundlich isotherm for adsorption of chlorophenol onto the activated sludge was shown in Fig. 9.

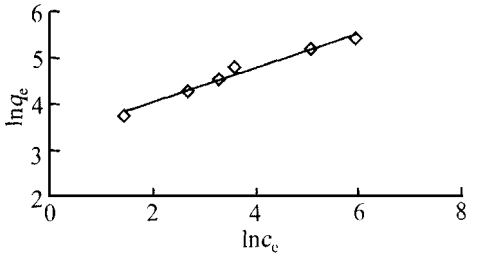

Fig. 9 Freundlich isotherm of chlorophenol adsorption

The values of constants K_F and $1/n$ were calculated by the least square method and also shown in Table 1. The constants of the Freundlich isotherm are not susceptible to as definite a physical interception on those in the case of Langmuir equation. However, K_F and $1/n$ give approximate measures of adsorbent capacity and intensity of adsorption, respectively. The Freundlich isotherm, although being an empirical equation, can be derived as the resultant of a large number of superimposed Langmuir equations, using a distribution of X_{max} and b values.

The high value of correlation coefficient (r^2) indicated a strong positive relationship between parameters. The constants X_{max}, which is a measure of the adsorption capacity to form a monolayer, can be as high as 237.3 mg/g. The constant b, which denotes adsorption energy, is equal to 0.027 mg^{-1}.

The Langmuir model makes several assumptions, such as monolayer adsorption and constant adsorption energy, while the Freundlich equation deals with physicochemical adsorption on heterogeneous surfaces. The agreement of the experimental data for chlorophenol adsorption by activated sludge with both these models implied that both monolayer adsorption and heterogeneous surface conditions existed under the experimental conditions used.

3 Conclusions

The ability of dried activated sludge to adsorb chlorophenol was investigated. The adsorption processes can be described by Langmuir and Freundlich isotherms. The maximum adsorption capacity achieved at initial pH of 1.0, however, the capacity was more than 80 mg/g when pH ranged from 1.0 to 10. The chlorophenol removal efficiency was more than 80% when the adsorbent dosage was> 2 g/L. The activated sludge may be used as a low-cost, natural and abundant bioadsorbent for the removal of chlorophenol from wastewater. It is an alternative to more costly materials such as granular activated carbon for removal of chlorinated phenols from waste streams.

References

[1] Kishino T, Kobayashi K. Relationship between the chemical structures of chlorophenols and their dissociation constants and partition constants in several solvent-water systems [J]. Wat Res, 1994, 28(7): 1547-1552.

[2] Pellizzetti Z, Marcrino V, Minero C, et al. Photocatalytic degradation of atrazine and other s-triazine herbicides [J]. Environ Sci Technol, 1990, 24(7): 1559-1565.

[3] Annachhatre A P, Gheewala S H. Biodegradation of chlorinated phenolic compounds [J]. Biotechnol Adv, 1996, 14(1): 35-56.

[4] Stephenson F A. Chemical oxidizers treat wastewater [J]. Environ Protec, 1992, 3(1): 23-27.

[5] White G C. Handbook of Chlorinatation and Alternative Disinfectants [M]. 3rd edn. Van Nostrand Reinhold, New York, 1992.

[6] Brasquet C, Roussy J Subrenat E. Adsorption and selectivity of activated carbon fibers application to organics [J]. Environ Technol, 1996, 17(8): 1243-1252.

[7] Binay K S, Narendra S R. Comparative sorption equilibrium studies of toxic phenols on fly ash and impregnated fly ash [J]. J Chem Technol Biotechnol, 1994, 61(2): 307-317.

[8] Kumar S, Upadhyay S N, Upadhyay Y D. Removal of phenols by adsorption on fly ash [J]. J Chem Technol Biotechnol, 1987, 37(2): 281-290.

[9] Kennedy K J, Lu J, Mohn W W. Bioadsorption of chlorophenols to anaerobic granular sludge [J]. Wat Res, 1992, 26(5): 1085-1092.

[10] Munaf E, Zein R, Kurniadi R. The use of rice husk for removal of phenol from wastewater as studied using 4-aminoantipyrine spectrophotometric method [J]. Environ Technol, 1997, 18(3): 355-358.

[11] Brandt S, Zend A, Deckwer W. Adsorption and desorption of pentachlorophenol on cells of *M. chlorophenolicum* PCP-1 [J]. Biotechnol Bioeng, 1997, 55(3): 480-491.

[12] Schuler M L, Kargi F. Bioprocess Engineering-Basic Concepts [M]. Prentice Hall, New Jersey, 1992.