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Effects of pH and temperature on isotherm parameters of chlorophenols biosorption to anaerobic granular sludge

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Abstract

As the most important parameters affecting the biosorption, pH and temperature were studied in this paper in order to more completely understand their effects on chlorophenols' biosorption onto anaerobic granular sludge. Sorption isotherms of 4-chlorophenol (4-CP) and 2,4-dichlorophenol (2,4-DCP) at various temperatures were determined; the data of 4-CP could be simulated by Langmuir model, while the data of 2,4-DCP could only be reproduced by Freudlich equation. The uptake capacity of 4-CP and 2,4-DCP could reach 1.5 mg g^{-1} and 5.04 mg g^{-1} when 2,4-DCP concentration was 90 mg L^{-1} and 4-CP concentration was 107 mg L^{-1}, respectively. 2,4-DCP was more strongly adsorbed onto the anaerobic granular sludge than 4-CP, which might be correlated with the numbers of chlorine substitute. The Experiments studying pH effects showed that the adsorption capacity of 4-CP and 2,4-DCP was quite pH dependent and increased with decrease in pH.

Keywords: Chlorophenol; pH; Temperature; Biosorption; Anaerobic granular sludge

1. Introduction

Chlorophenols (CPs) are the most common organic pollutants that used widely in agriculture, industry and public health. The most important pollution sources containing chlorophenols are the wastewaters from pesticide, paint, solvent, pharmaceutics, wood preserving chemicals, paper and pulp industries and water disinfecting process. Because, CPs are toxic, resistant to microbial degradation, and can accumulate in the food chain, many countries have restricted or banned the production or use of CPs and designated them as priority pollutants in their own list of hazardous wastes [1,5].

The traditional methods used in the treatment of CPs include physical treatment like activated carbon adsorption, hyperfiltration, solvent extraction, reverse osmosis, etc.; chemical treatment like chemical oxidization, incineration, chemical degradation, wet oxidation, hypercritical oxidation, UV/H_2O_2 method, TiO_2 photochemical oxidation, high-pressure impulsive discharge, low temperature plasma, high frequent ultrasonic method, etc.; biological treatment like activated sludge, membrane separation technique, aerobic/anaerobic method, etc. The development of traditional physical and chemical methods are limited because of their high cost, in addition, the efficiency of traditional biological methods is not satisfying because of CPs' structural stabilization and toxicity [2–5]. So some new and alternate methods should be developed.

Biosorption is a kind of promising technique that can accumulate CPs from wastewater because of its great adsorption result, high selectivity, low cost and satisfied removal efficient. Some kinds of biomass like algae, waste bacteria from fermentation industry and activated sludge over grown in wastewater systems can be separated and utilized for removal of CPs as an abundant and cheaper biosorbent, which reduce the treatment cost to great extent and make the wastes reused [6]. Meanwhile, there is no need to add nutrients to the chlorophenol treatment systems because many researchers found dead biomass can also remove CPs dramatically and their adsorption capacities are no more than the live during the short adsorption time [6–10]. These advantages have led many workers to do some research on it. The present studies focus on searching for more economic, practical and efficient adsorbent, and studying their biosorption capacity, investigating the parameters affecting biosorption efficiency and figuring out their biosorption mechanisms [6–16].

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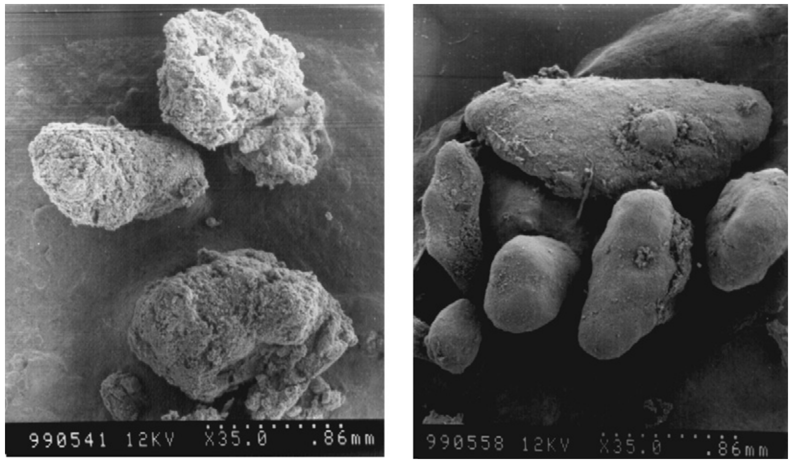

Fig. 1. Granular anaerobic sludge appearance.

Biosorption of CPs by anaerobic sludge and some other biomass has received increasing attention in recent years [9,10,14,16,18,19]. Anaerobic granular sludge is a biomass contained greatly in anaerobic wastewater treatment reactors (UASB, ABR, etc.), which mainly consists of bacteria and protozoa. They can adsorb components through their outer membranes which are mainly archaebacteria (methanogens) and consists of squalene and ether linked polar lipids [9].

As hydrophobic organic pollutants like CPs show a high tendency to accumulate into microbial cells and sludge, the biosorption or accumulation of these hazardous pollutants may bear a significant consequence as it might serve as the first step in introducing such toxic chemicals into the food chain [2]. So an assessment of this biosorption process would help to understand the environmental fate, transport and bioavailability behavior of CPs in water body.

In this study, the sorption behavior of 4-CP and 2,4-DCP on anaerobic granular sludge was studied. Particular attention was paid to the effects of two parameters like pH and temperature. The sorption capacities were compared at different temperatures, the suitability of Freudlich and Langmuir equilibrium equation were investigated, the relationship between the sorption capacity of CPs and pH value was also given.

2. Materials and methods

2.1. Sorbent, reagents and solutions

Anaerobic granular sludge used in this study was collected from the ABR (anaerobic baffle reactor) of the lab of Tsinghua University. The cells were centrifuged at 5000 rpm for 5 min, washed with sterile distilled water three times, homogenized in a homogenizer at 8000 rpm for 20 min, and then stored in the refrigerator. The cell density was determined as 19–20 g L^{-1}. Fig. 1 shows the typical appearance of granular sludge used in this study.

Two chlorinated phenols, including 4-chlorophenol and 2,4-dichlorophenol (analytical grade) were used in this study. HPLC-grade compounds were prepared as 1 g L^{-1} stock solutions in 0.01 mmol L^{-1} NaOH, which were further diluted to standard solutions. The experimental aqueous solutions of CPs were prepared by diluting the solutes, or other solutions, in deionized water to the required concentrations.

2.2. Sorption experiments

Adsorption equilibrium experiments were conducted by adding 5 ml stock solution of anaerobic granular sludge to 50 ml Erlenmeyer flasks containing 10 ml of aqueous solution of different CPs with pH values ranging from 2.15 to 11.18, then the aqueous solutions were sealed and shaken at 150 rpm for 6 h to ensure equilibrium was reached [2,9] at designated temperature. Samples were taken after equilibrium had been reached. Before analysis, samples were centrifuged at 8000 rpm for 10 min, the supernatant fluid filtered immediately through 0.45 μm membranes. The second 2 ml of the filtrate was collected into a sample bottle and stored at 4 °C until analysis. The concentration range of 4-CP varied between 10 and 107 mg L^{-1}, and the concentration range of 2,4-DCP varied between 9 and 90 mg L^{-1}.

Experiments conducted to study pH effects were performed at a constant temperature of 25 °C to represent environmental condition with 90 mg L^{-1} initial concentration of 4-CP and 2,4-DCP.

Uptake capacity at equilibrium, q_e (expressed as mg g^{-1} anaerobic granular sludge), was calculated by Eq. (1):

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

where C_e (mg L^{-1}) is the aqueous-phase adsorbate concentrations at equilibrium, C_0 the initial aqueous-phase adsorbate concentration, V the volume of the solution (L), and W is the mass of anaerobic granular sludge (g).

2.3. Analysis of chlorophenols

The concentration of residual 4-CP and 2,4-DCP in the sorption medium was determined with an HPLC system. Separations were achieved on a waters reverse-phase C18 analytical column at 270 nm for 4-CP and 284 nm for 2,4-DCP. Each sample was

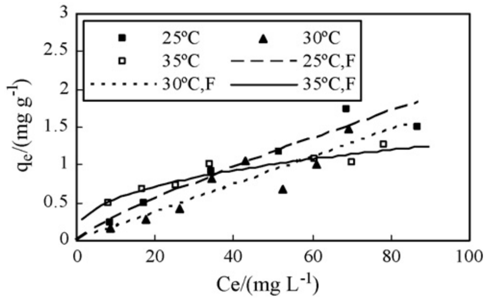

Fig. 2. Effect of temperature on 4-CP biosorption (T = 25, 30, and 35 °C; Initial pH 6.5; v, 150 rpm; equilibrium time, 6 h).

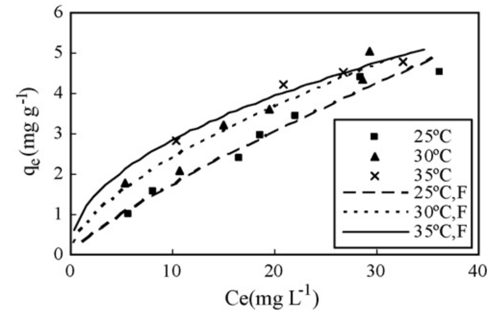

Fig. 3. Effect of temperature on 2,4-DCP biosorption (T = 25, 30, and 35 °C; Initial pH 6.5; v, 150 rpm; equilibrium time, 6 h).

tested two times and the average values were used for further analysis.

3. Sorption isotherms models [5,6]

Adsorption is a well-known equilibrium separation process. There are many isotherm equations used for modeling the adsorption equilibrium, such as Langmuir, Freundlich, linear and Redlich-Peterson equation, etc. [6]. Among all of these, Langmuir and Freundlich are the most widely used equations. In this study, equilibriums were described by these two classical models of monolayer sorption.

The Freundlich model is an empirical equation based on sorption on a heterogeneous surface and expressed by Eq. (2):

$$q_e = K_F {C_e}^{1/n} \tag{2}$$

where K_F and n are the Freundlich coefficients. K_F and n are indicators of adsorption capacity and adsorption intensity, respectively.

The Langmuir model is another popular used equation, because its coefficients have some real meanings. Langmuir equation is valid for monolayer sorption on to a surface with a finite number of identical sites and its expression is given by Eq. (3):

$$q_e = q_m \frac{bC_e}{1 + bC_e} \tag{3}$$

where q_m and b are the Langmuir coefficients. q_m the maximum amount of the pollutant per unit weight of adsorbent to form a complete monolayer on the surface bound at high C_e (mg g^{-1}), and b is a constant related to the affinity of the binding sites (L mg^{-1}). q_m and b can be determined from the linear plot of $1/q_e$ vd $1/C_e$.

4. Results and discussion

4.1. Effect of temperature

Figs. 2 and 3 describe the effects of temperature on the 4-CP and 2,4-DCP uptake capacities at 25, 30 and 35 °C. The results in both figures showed that the adsorption capacities of 4-CP and 2,4-DCP increased with the increasing of C_e, while the tendency of increasing became slow. These phenomena could be explained as the adsorption sites on the mass unoccupied were gradually taken till saturation by CPs with increasing of the CPs' concentration under the same amount of biomass.

Meanwhile, to understand effects of temperature on the maximum adsorption capacities of CPs by anaerobic granular sludge, the calculated lines using Freundlich model were also drawn in Figs. 2 and 3. The tendency of lines under different temperatures showed that the maximum uptake capacities increased with temperature decreasing from 35 °C to 25 °C for 4-CP and 2,4-DCP, which indicated the adsorption processes of 4-CP and 2,4-DCP by anaerobic granular sludge were exothermic. This study drew the same conclusion with Kennedy [9]. The uptake capacity of 4-CP and 2,4-DCP could reach 1.5 mg g^{-1} and 5.04 mg g^{-1} under the concentration range studied, respectively.

Comparison between Figs. 2 and 3 indicated that 2,4-DCP was more strongly adsorbed than 4-CP under the same condition, which might be correlated with the numbers of chlorine substitute. This drew the same conclusion with many researchers who found the fact that the increasing number of chlorine substituents leads to increase in the acidity and hydrophobicity (K_{ow}) and decrease in the solubility, and that the binding capacity is directly proportional to the hydrophobicity and inversely to the solubility [17,19]. Wu et al. [17] found that the sorption capacities of 4-CP and 2,4-DCP on mycelial pellets was in the order of: 4-CP < 2,4-DCP which increased with decreasing water solubility and increasing octanol–water partitioning coefficient, hydrophobicity might govern the biosorption of phenolic compounds by fungal mycelia biomass.

Fig. 4 shows 4-CP and 2,4-DCP adsorption capacities of this study and the results of previous work reported by Kennedy [14] under 35 °C. From Fig. 4, it was easy to tell this study got the

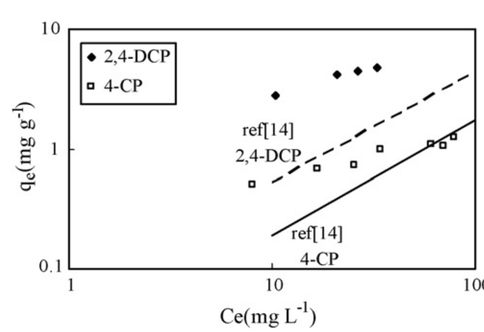

Fig. 4. Comparison of the results in this study with that reported by Kennedy (T = 35 °C; v, 150 rpm; equilibrium time, 6 h).

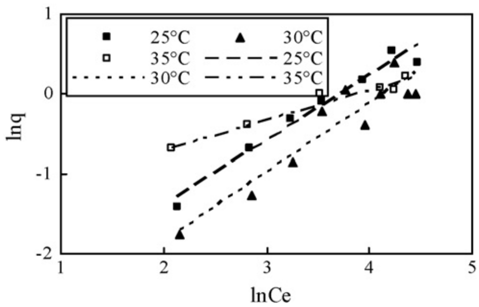

Fig. 5. Freundlich isotherm equations of 4-CP at various temperatures.

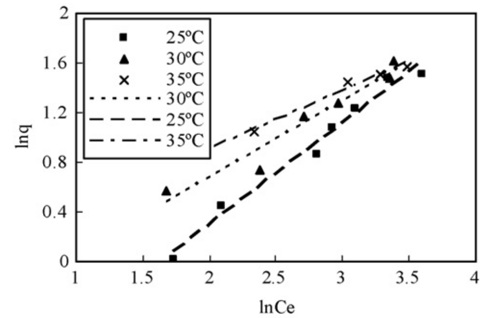

Fig. 7. Freundlich isotherm equations of 2,4-DCP at various temperatures.

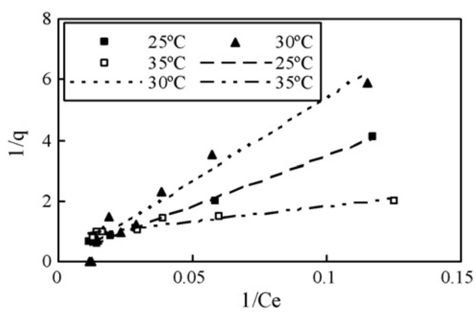

Fig. 6. Langmuir isotherm equations of 4-CP at various temperatures.

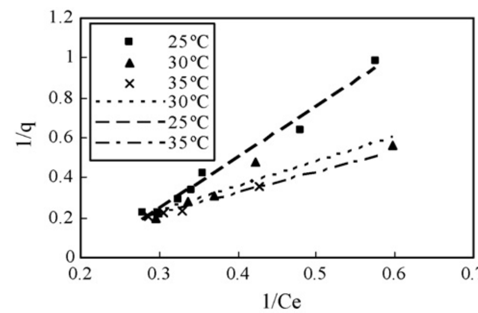

Fig. 8. Langmuir isotherm equations of 2,4-DCP at various temperatures.

similar results with Kennedy's and there did not exist differences in the order of magnitude.

4.2. Freundlich and Langmuir adsorption isotherms at various temperatures

Adsorption isotherms are plots between the sorption uptake and the final equilibrium concentration of the residual sorbate remaining in the solution. To simulate the results, many adsorption isotherm equations have been developed [6]. Among these equations, Freundlich and Langmuir are the most popular ones. To investigate the suitability of these two equations, they were applied in the results of this study. Figs. 5–8 show Freundlich and Langmuir adsorption isotherms of 4-CP and 2,4-DCP at three temperatures ($T=25$, 30, and 35 °C), and the simulated equations were given in Table 1.

Table 1 shows that the equilibrium data of 4-CP can be simulated by Langmuir isotherm quite well, but as for 2,4-DCP, Langmuir was not a suitable model because the intercept of equations was negative from which q_m values could not be calculated. Freundlich equation could simulate experiment data of 2,4-DCP quite well. The calculated line using Freundlich model drawn in Fig. 1 also proved this point.

To investigate the relationship between temperature and parameters of Freundlich and Langmuir equation, parameters calculated according to Freundlich and Langmuir expression were given in Table 2. Langmuir equation parameters of 4-CP showed that the maximum uptake capacities decreased from 6.2171 mg g^{-1} to 1.2610 mg g^{-1} with increase in temperature, while as for 2,4-DCP, K_F and n values of Freundlich equation increased positively with temperature.

4.3. Effect of pH

Among the factors affecting the biosorption of CPs on anaerobic granular sludge, pH is the most critical one because it can affect the degree of ionization of CPs and the surface properties of the biosorbent. Many researchers studied its effects [5,11–13].

Table 1
Langmuir and Freundlich equations of 4-CP and 2,4-DCP at various temperatures

T (°C)	Freundlich equation	Langmuir equation
4-CP		
25	$\ln q = 0.817, 8 \ln Ce - 3.0482$ ($R^2 = 0.9695$)	$1/q = 32.872/C_e + 0.1583$ ($R^2 = 0.9952$)
30	$\ln q = 0.9655 \ln Ce - 3.8893$ ($R^2 = 0.816\,4$)	$1/q = 50.678/C_e + 0.1734$ ($R^2 = 0.9505$)
35	$\ln q = 0.3753 \ln Ce - 1.4608$ ($R^2 = 0.941\,5$)	$1/q = 10.12/C_e + 0.793$ ($R^2 = 0.9261$)
2,4-DCP		
25	$\ln q = 0.8178 \ln Ce - 1.3405$ ($R^2 = 0.9804$)	$1/q = 2.5329/C_e - 0.5144$ ($R^2 = 0.9837$)
30	$\ln q = 0.6148 \ln Ce - 0.5443$ ($R^2 = 0.9407$)	$1/q = 1.2179/C_e - 0.1276$ ($R^2 = 0.8953$)
35	$\ln q = 0.4686 \ln Ce - 0.0338$ ($R^2 = 0.9772$)	$1/q = 1.0469/C_e - 0.098$ ($R^2 = 0.9896$)

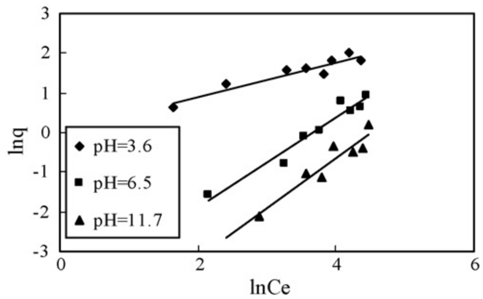

Fig. 9. The Freundlich isotherms of 4-CP at various pH.

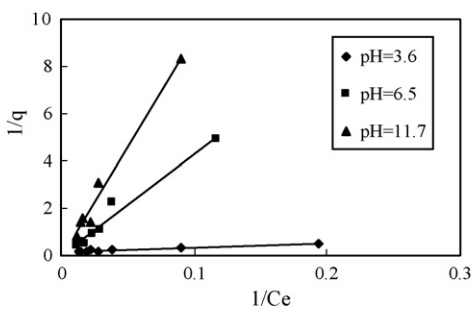

Fig. 10. The Langmuir isotherms of 4-CP at various pH.

To verify the results drawn by the former workers and understand its effects extensively, similar studies were conducted in this paper.

Figs. 9 and 10 and Table 3 show the Freundlich, Langmuir isotherm equations of 4-CP at three pH values (pH = 3.6, 6.5, and 11.7) and relationship between pH and parameters of Langmuir, Freundlich equation of 4-CP at 25 °C. The results showed that Langmuir, Freundlich equations both fitted the data quite well, and the former fitted better (${R_L}^2 > {R_F}^2$). Figs. 8 and 9 also indicated that the uptake capacity of 4-CP to anaerobic granular sludge increased with decrease in pH. The data in Table 3 show the values of parameters of Freudlich isotherm equation (K_F and n) increased with decrease in pH. In Freundlich equation, K_F is an indicator of sorption capacity and n indicates sorption intensity. K_F and n values increased with decrease in pH meant that 4-CP had greater sorption capacity and bind onto anaerobic granular sludge to a greater extent at lower pH. q_m values of Langmuir equation that decreased from 7.776 mg g^{-1} to 1.0340 mg g^{-1} with increase in pH also drew this conclusion.

To understand effect of pH on the biosorption of 4-CP and 2,4-DCP on anaerobic granular sludge in a wider range, several pH values in the range of 2–12 were applied in this study. Fig. 11 shows the relationship between pH and equilibrium uptake capacities (q_e) of 4-CP and 2,4-DCP. Figure showed that the uptake capacity of anaerobic granular sludge for 4-CP and 2,4-DCP were similar at pH 2.0 and 3.0, while the uptake capacity for 2,4-DCP was greater than that for 4-CP for the pH values greater than 3.0. This might be explained by effect of pH on affinity forces between the sorbent and sorbate.

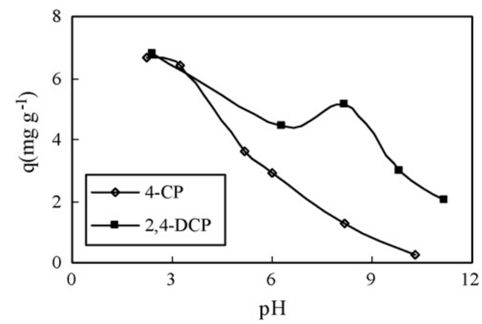

Fig. 11. The relationship between pH and biosorption capacities of 4-CP and 2,4-DCP (T = 25 °C).

Table 3
The parameters of Langmuir, Freudlich equations of 4-CP at various pH (T = 25 °C)

pH	Freudlich equation			Langmuir equation		
	K_F	$1/n$	R^2	q_m (mg g^{-1})	b (L mg^{-1})	R^2
3.6	0.9866	0.4614	0.8675	7.7760	0.0640	0.9452
6.5	0.0474	0.8187	0.9695	6.3171	0.0048	0.9952
11.7	0.0033	1.2716	0.9049	1.0340	0.0060	0.9594

pH primarily affects the degree of ionization of the phenolic sorbate and the surface properties of the biosorbent, i.e., surface charge of the cells. When pH is not more than one unit above pK_a values of CPs (4-CP: pK_a = 9.18, 2,4-DCP: pK_a = 7.89) [14], the contribution of phenolate sorption is practically negligible as reported by previous study [17]. Non-dissociated form activated by the OH^- and Cl^- dominated the overall sorption of chlorinated phenols on organic sorbents. When pH is greater than pK_a values of CPs, negatively charged ionized forms dominate in the solution.

Surface properties of anaerobic sludge are also affected by pH. When pH is lower than isoelectric point of biomass (the isoelectric point of anaerobic sludge would be usually between pH 1 and 3) [18], the overall surface charge on the cells became

Table 2
The parameters of Freundlich and Langmuir equation at various temperature

T (°C)	Freundlich equation			Langmuir equation		
	2,4-DCP			4-CP		
	K_F	$1/n$	R^2	q_m (mg g^{-1})	b (L mg^{-1})	R^2
25	0.2617	0.8178	0.9804	6.3171	0.0048	0.9952
30	0.5802	0.6148	0.9407	5.7372	0.0034	0.9505
35	0.9668	0.4686	0.9772	1.2610	0.0784	0.9261

positive and this led to the interactions between the aromatic ring of 4-CP and 2,4-DCP activated by the OH^- and Cl^-, and the groups of the biosorbent surface. At very low pH values, the surface of sorbent would also be surrounded by the hydronium ions which enhance the chlorinated phenols interaction with binding sites of the biosorbent by greater attraction forces [5]. These affinity forces was so powerful that the uptake capacity of 4-CP and 2,4-DCP was mainly related to their initial concentrations at very low pH values. As the pH was increased, the overall surface charge on the cells became negative and the biosorption between negatively charged CPs and binding sites of the biomass surface decreased.

There was an increase in the uptake capacity of 2,4-DCP at pH 8.0 (Fig. 11), while there was not for 4-CP. This phenomena could not be explained by the proposed biosorption mechanisms due to the initial pH, so there might be some other types of mechanisms such as ion exchange, complex formation or electron share, membrane transport and physico-chemical forces such as van der Waals, H-binding, etc., like other researchers proposed [5,6,14,18].

5. Conclusions

The effects of pH and temperature on the biosorption of 4-CP and 2,4-DCP on anaerobic granular sludge were investigated in this paper. The results showed that pH and temperature were the most critical factors affecting uptake capacity. Sorption isotherms of 4-chlorophenol (4-CP) at various temperatures and pH values showed that the data of 4-CP could be simulated by Langmuir model, while the data of 2,4-DCP could only be reproduced by Freudlich equation. 2,4-DCP was more strongly adsorbed onto the anaerobic granular sludge than 4-CP, which might be correlated with the numbers of chlorine substitute or hydrophobicity of CPs. The experiments studying pH effects showed that the adsorption capacity of 4-CP and 2,4-DCP increased with decrease in pH, but there was an increase in the uptake capacity of 2,4-DCP at pH 8.0.

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References

[1] J. Wang, Immobilized Microbial Technology and Water Pollution Control, Science Press, Beijing, 2002, pp. 248-300 (in Chinese).
[2] J. Wang, Y. Qian, N. Horan, Ed. Stentiford, Bioadsorption of Pentachlorophenol (PCP) from Aqueous Solution by Activated Sludge Biomass, Biores. Technol. 75 (2000) 157–161.
[3] A. Krishnaiah, Adsorption of phenol and *p*-chlorophenol from their single and bisolute aqueous solutions on Amberlite XAD-16 resin, J. Hazard. Mater. B105 (2003) 143–156.
[4] M.-W. Jung, K.-H. Ahn, Y. Lee, K.-P. Kim, J.-S. Rhee, J.T. Park, K.-J. Paeng, Adsorption characteristics of phenol and chlorophenols on granular activated carbons (GAC), Microchem. J. 70 (2001) 123–131.
[5] Z. Aksu, J. Yener, A comparative adsorption/biosorption study of monochlorinated phenols onto various sorbents, Water Manage. 21 (2001) 695–702.
[6] Z. Aksu, Application of biosorption for the removal of organic pollutants: a review, Process Biochem. 40 (2005) 997–1026.
[7] P. Benoit, E. Barriuso, R. Calvet, Biosorption characterization of herbicides, 2,4-D and atrazine, and two chlorophenols on fungal mycelium, Chemosphere 27 (7) (1998) 1271–1282.
[8] A. Denizli, N. Cihangir, N. Tüzmen, G. Alsancak, Removal of chlorophenols from aquatic systems using the dried and dead fungus Pleurotus sajor caju, Biores. Technol. 96 (2005) 59–62.
[9] K.J. Kennedy, T.T. Pham, Effect of anaerobic sludge source and condition on biosorption of PCP, Water Res. 29 (10) (1995) 2360–2366.
[10] Z. Ning, L. Fernandes, K.J. Kennedy, Chlorophenol sorption to anaerobic granules under dynamic conditions, Water Res. 33 (1) (1999) 180–188.
[11] X. Lu, X. Zhang, F. Qu, X. Gu, Study on adsorption performance of activated sludge to chloro-aromatic-compound in biological treatment process, Environ. Chem. 33 (6) (1998) 649–655 (in Chinese).
[12] Z. Aksu, J. Yener, Investigation of the biosorption of phenol and monochlorinated phenols on the dried activated sludge, Process Biochem. 33 (6) (1998) 649–655.
[13] G.M. Sinclair, G.I. Paton, A.A. Meharg, K. Killham, Lux-biosensor assessment of pH effects on microbial sorption and toxicity of chlorophenols, FEMS Microbiol. Lett. 174 (1999) 73–278.
[14] K.J. Kennedy, J. Lu, W.W. Mohn, Biosorption of chlorophenols to anaerobic granular sludge, Water Res. 26 (8) (1992) 1085–1092.
[15] Y. Chen, S. Yan, Q. Sun, Z. Jin, The relationship between biosorption characteristics and structure of phenolic compounds, China Environ. Sci. 18 (3) (1998) 248–251 (in Chinese).
[16] L. Hao, Y. Zhou, H. Zhang, Biosorption, desorption and biodegradation of pentachlorophenol (PCP) by anaerobic granular sludge in an upflow anaerobic sludge blanket (UASB) reactor, China Environ. Sci. 19 (1) (1999) 5–8 (in Chinese).
[17] J. Peuravuorio, N. Paaso, K. Pihlaja, Sorption behavior of some chlorophenols in lake aquatic humic matter, Talanta 56 (2002) 523–538.
[18] Z. Aksu, D. Akpinar, Competitive biosorption of phenol and chromium(VI) from binary mixtures onto dried anaerobic activated sludge, Biochem. Eng. J. 7 (2001) 183–193.
[19] J. Wu, H.-Q. Yu, Biosorption of phenol and chlorophenols from aqueous solutions by fungal mycelia, Process Biochem. 41 (2006) 44–49.