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Adsorption of phenolic compound by aged-refuse

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Abstract

The adsorption of phenol, 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol by aged-refuse has been studied. Adsorption isotherms have been determined for phenol, 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol and the data fits well to the Freundlich equation. The chlorinated phenols are absorbed more strongly than the phenol and the adsorption capacity has an oblivious relationship with the numbers and the position of chlorine subsistent. The experiment data suggests that both the partition function and the chemical adsorption involve in the adsorption process. Pseudo-first-order and pseudo-second-order model were applied to investigate the kinetics of the adsorption and the results show that it fit the pseudo-second-order model. More than one step involves in the adsorption process and the overall rate of the adsorption process appears to be controlled by the chemical reaction. The thermodynamic analysis indicates that the adsorption is spontaneous and endothermic.

Keywords: Adsorption; Phenol; Refuse; Biofilter

1. Introduction

A biofilter with aged-refuse as the filling used to treat landfill leachate, phenolic compounds wastewater, coking wastewater and livestock wastewater has been studied in our previous work [1–6]. A satisfactory result was obtained in terms of recalcitrant pollutants removal and cost reduction in comparison with traditional methods.

Adsorption and biodegradation are the mechanism leading to the removal of recalcitrant pollutants from effluent wastewater. The adsorption–biosorption of organic pollutants has been shown to play a key role in the final fate of organic pollutants. Adsorption of organic pollutants on the biologically inactive materials such as activated carbon used as a pretreatment method in integrated biological-chemical treatment process have been addressed in some studies [7]. The adsorption and accumulation of various organic pollutants by live and dead biomass in conventional biological treatment process when insufficient contact time is available have also been studied in detail by the authors [8,9].

In biofilter with aged-refuse as the filling, the high adsorption capacity, biomass inventory and long contact time make adsorption–biodegradation of the organic pollutants in balance and so that the effective removal become possible. While very little is known about the fate of organic pollutants after discharged into the biofilter. The adsorption process, as well as its role in the whole process of removal pollutants from wastewater by biofilter has not been addressed in our previous study. With a aim to develop cost-effective treatment technology for organic pollutants by biofilter, a better understanding of the adsorption process and mechanism that affect the fate of the organic pollutants in the biofilter are required. This work investigated the adsorption process of organic pollutants by the aged-refuse in the biofilter and developed a model to predict the adsorption of organic pollutants with phenol, 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol as model compounds. The results of the adsorption tests can be used to estimate the concentration of organic pollutants adsorbed to the aged-refuse in biofilter. The data obtained from this study can improve our understanding on the fate of organic pollutants in biofilter and which is a key step to developing an effective method to remove the organic pollutants by biofilter.

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Table 1
Characterization of aged-refuse

Disposed time (year)	Water content (%)	Organic content (%)	pH	TN (%)	TP (%)	CEC (meq/100 g)	Specific surface area ($m^2\ g^{-1}$)
1990	34.0	9.69	7.65	0.41	1.02	68.7	5.46
1994	27.5	10.47	7.42	0.76	1.18	71.4	3.78

Table 2
The total number of bacteria in aged-refuse and in comparison with other soil

Samples	The total number of bacteria (per gram of dried sample)
Aged-refuse	8.63×10^6
Aged-refuse	9.02×10^6
Red earth	11.03×10^6
Cabook	5.07×10^6
Rice soil	32.30×10^6

2. Materials and methods

2.1. Aged-refuse

2.1.1. Aged-refuse resource

All the aged-refuse used in this study was sampled from Shanghai Laogang landfill disposed in 1990 and 1994, respectively. The aged-refuse was taken to the laboratory and then naturally air-dried at laboratory. The larger inorganic substances, such as stones, glass, bottles, etc., were separated and removed. After screened by a conventional mechanical screener and the size less than 15 mm diameter was used as the filling in biofilter. Aged-refuse used as adsorption experiment was collected from biofilter for consecutive treating phenolic compounds, the biofilter set-up and the operation mode have been described elsewhere [1,2].

2.1.2. Characterization of the aged-refuse

For further basic characteristics analysis, the age-refuse was broken into small pieces by hammer or ball miller. At least 10 kg aged-refuse was sampled and the characteristics of the aged-refuse, such as water content, organic content, CEC, pH, TP, TN, specific surface area and total number of bacteria were measured in triplicate. The result is shown in Tables 1 and 2.

2.1.3. Leaching test

In order to evaluate that if the aged-refuse brings second pollution to the environmental, the content of the heavy metal and the leaching test of the aged-refuse have been conducted in this study. The leaching tests method as follows:

(1) Fifty grams aged-refuse less than 15 mm was put in to the poly propylene container and add the water until to get the liquid/solid ratio of 10 before adjust the pH value to 5.8–6.3 with sodium hydroxide or nitric acid.
(2) The container was agitated on a controlled temperature shaker at a 110 rpm of constant shaking rate for 8 h and then stabilized for 16 h.
(3) Filtered by mediate speed-quantitative filter paper.
(4) The filtrate was measured by ICP. The leaching test was conducted in duplicate and the concentration of heavy metal was measured in triplicate. All the data is shown in Tables 3 and 4.

2.2. Adsorption experiment

2.2.1. Chemical reagents

All the experiment solutions were prepared by diluting 1.0 g/dm^{-3} of stock solution of all the phenolic compounds to the desired concentration. A stock solution was obtained by dissolving 1.0 g of all the tested compounds of analytical reagent grade in 1 dm^{-3} distilled water. The concentration of all the tested compounds ranges from 100 to 500 mg/l.

2.2.2. Batch adsorption test

Adsorption experiments were conducted in a routine manner by the batch technique. Five grams aged-refuse shakes up with a 100 ml phenol solution of different concentrations in a flask. Before mixing the refuse with the tested solution, the initial pH value of each test was adjusted to the desire value by dilute solution of hydrochloric acid and sodium hydroxide solutions, respectively. The flasks were agitated on a controlled temperature shaker at a 150 rpm of constant shaking rate. Background samples containing aged-refuse and no samples and controls

Table 4
Heavy metal concentration of leaching test in aged-refuse (mg/kg)

	Refuse (1990)
As	0.22
Pb	0.25
Cr	0.11
Cd	0.02
Ni	0.95
Cu	0.82
Zn	0.94
Hg	0.02

Table 3
Heavy metal concentration of in aged-refuse (mg/kg)

	As	Pb	Cr	Cd	Ni	Cu	Zn	Hg
Refuse (1990)	138.60	285.14	152.56	0.58	50.10	178.53	652.88	1.18
Soil stand (GB 5618-1995)	400	500	300	1.0	200	400	500	1.5

containing sample but no aged-refuse also run at the same condition. The control experiments were used to evaluate the stripping of the aged-refuse and the possibility of volatilization and biodegradability of phenolic compounds. All the experiments were carried out in duplicates and average values were used for further conclusions.

2.2.3. Analysis

At the end of the equilibrium time, liquid phase was separated from the aged-refuse by centrifuged at 3000 × *g* for 30 min. The solid phase was washed with distilled water and the washing water was added to the liquid phase. Phenolic compounds concentration in the liquid phase determined by the methods of spectrophotometer. The concentration of phenolic compounds adsorbed to the aged-refuse was calculated as the difference between initial and phenolic compounds concentration in the liquid phase. The leaching test was conducted in duplicate and the concentration of phenolic compounds was measured in triplicate.

3. Result and discussion

The effects of contact time, initial pH and initial concentration on the adsorption equilibrium of the tested compounds on the aged-refuse have been investigated. The results are given as the unit of adsorption quantity per gram adsorbent in given time and equilibrium.

3.1. Characterization of the aged-refuse

As shown in Tables 1 and 2, the characteristics of the aged-refuse do not varied greatly with the disposed time. It is agreement with our previous work reported that the refuse will become chemical and biological stabilized after it had been disposed for 8 years. The organic content of aged-refuse disposed in 1990 and 1994 was measured as 9.69 and 10.47%, respectively, and it almost equals to that of fertile soil and higher than that of general sand soil. The CEC of the aged-refuse disposed in 1990 and 1994 is more than ten times that of general soil and two or three times that of fertile soil. The total number of biomass in aged-refuse of 1990 and 1994 almost equals to that of fertile soil. The high organic content, CEC and the wide and larger quantity of biomass contribute the high adsorption capacity of aged-refuse.

3.2. Leaching test

The content of As, Pb, Cd, Hg, Zn, Cu, Ni, Cr in aged-refuse is shown in Table 3, all the heavy metal can get the soil stand (GB 5618-1995) permissible limit except that the content of Zn is a little higher. As shown in Table 4 that the leaching solution contain a very negligible amount of heavy metal and are not so sufficiently high to bring second pollution to the environment.

3.3. Effect of contact time

The adsorption rate of organic pollutants by biomass or other adsorbents is very rapid and the adsorption equilibrium can reach

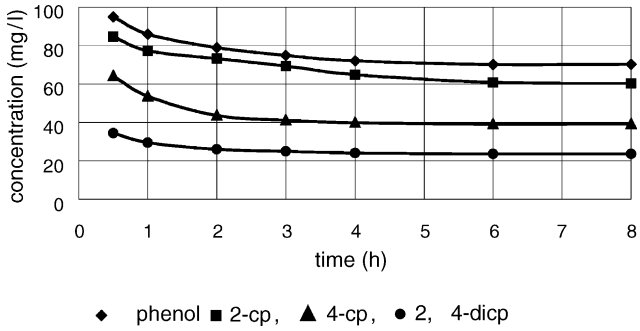

Fig. 1. Equilibrium time for adsorption of phenolic compound by refuse.

in less than 24 h [8,10,11]. The adsorbent in this study is quite different from those used by the above investigators because it includes not only the aged-refuse but also the biomass. The data for the adsorption of phenolic compounds versus contact time is shown in Fig. 1. The results show that the adsorption of phenolic pollutants in aqueous solutions by aged-refuse was very rapid because the largest amount of phenol was removed with in the first 2 h. The remaining concentration of the phenolic pollutants in the liquid phase become asymptotic to the time axis after 4 h of shaking and the adsorption equilibrium was reached in less than 6 h. The rapid adsorption of phenolic compounds to aged-refuse ensures that sufficient time is available for adsorption equilibration to get at the usual operator condition of the biofilter. However, for subsequent experiment, the samples were left for 12 h to ensure the adsorption equilibrium. The equilibrium time of different initial concentration of all the phenilic compounds was also conducted and the result shows that initial concentrations of phenolic pollutants have little effect on the adsorption equilibrium time.

3.4. Effects of pH

The pH value of the adsorption medium is the most critical parameter that affects the adsorption capacity of aged-refuse. The adsorption of phenolic compound by aged-refuse was studied at different initial pH values of 3–9. The pH before and after adsorption process was also measured and found that the difference between the two measured values of pH was less than 0.2. The variation of equilibrium adsorption capacity of all the tested pollutants with different initial pH is shown in Figs. 2–5.

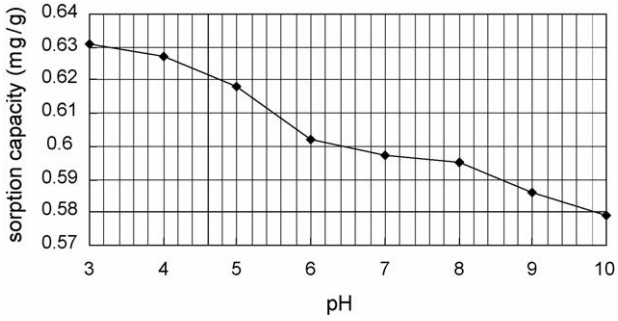

Fig. 2. The influence of pH value on the sorption capacity of phenol.

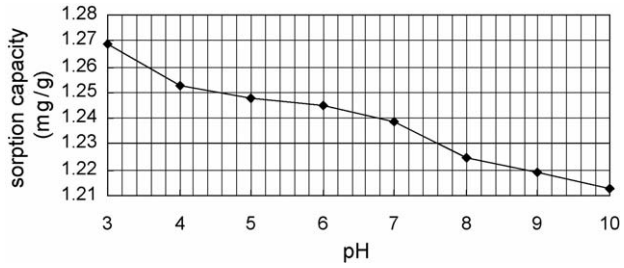

Fig. 3. The influence of pH value on the sorption capacity of 2-chlorophenol.

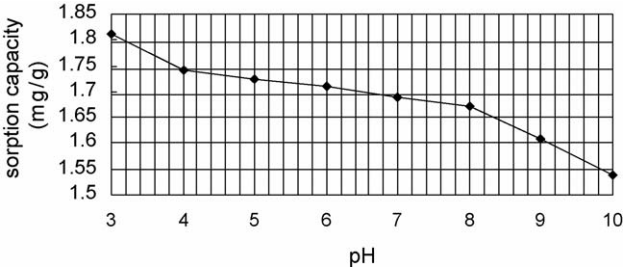

Fig. 4. The influence of pH value on the sorption capacity of 4-dichlorophenol.

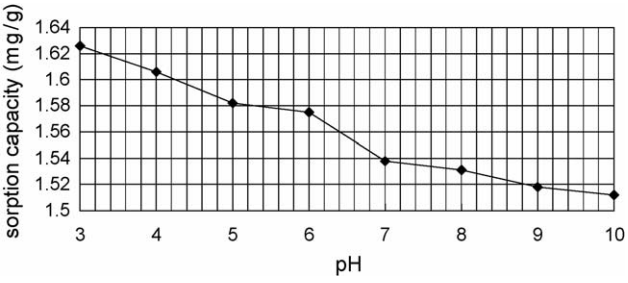

Fig. 5. The influence of pH value on the sorption capacity of 2,4-dichlorophenol.

As shown in Fig. 2 that the adsorption capacity of all the phenolic compounds decreases with increasing the pH value. This can be attributed to the pH value affecting the degree ionization of the phenolic compounds. The ionic fraction of phenolic compounds can be calculated from $I = [A^-]/[HA] = K_a/[H^+] = 10^{(pH-pK_a)}$. When $pH = pK_a$, the anions form and neutral form will be 50%, respectively, with the increase of the pH, the anion form increases while neutral form decreases. The neutral form can be neglected when $pH > pK_a$ more than 2 units. Compared with the pK_a value of the phenolic compounds in Table 5, it can be found that the pK_a value decrease with the increase number of the chlorine atoms substituted and also with the closing of the chlorine atom position to the OH group in chlorophenols having the same number of chlorine atoms substituted. Phenol, 2-chlorophenol, 4-chlorophenlp and 2,4-dichlorophenol have quite different ratio of anions form at the same pH value owning to their different pK_a value. The adsorption capacity of phenol decrease rapidly with the $pH > 8$, it is because the neutral form of phenol will decrease greatly and limit the adsorption of phenol in the organic matter of aged-refuse by partition function. Another reason is that with the increase the pH, more and more humic substances, especially humic acids, will get into the water from aged-refuse and hence decreases the phenolic adsorption capacity by the aged-refuse. As the same reason, for 2,4-dichlorophenol, the adsorption capacity decreases rapidly when $pH > 6$.

In addition, pH also affects the surface property of the biomass and hence influences the equilibrium adsorption process. At lower pH, the overall surface charge of the biomass become positive and this leads to donor–acceptor interactions between the aromatic ring of the phenolic compound, especially chlorinated phenol activated by the –Cl, and the surface of the biomass [12]. At very lower pH values, the surface of the biomass will be surrounded by the hydrogen ion and which enhance the chlorinated phenols interaction with the biomass with attractive force. As the pH increases, however, the overall surface charge of aged-refuse becomes negative and the repulsive forces prevailing, hence the adsorption capacity decreases.

3.5. Adsorption isotherms

Several models have been reported in the literature to describe experimental data of adsorption isotherms. The Freundlich model has been widely adopted to characterize the adsorption of organic pollutants from water and it was also used to fit the adsorption data in this study.

The linear form of the Freundlich isotherm model is given by the following equation.

$$\ln q_e = \left(\frac{1}{n}\right) \ln C_e + \ln K \quad (1)$$

where q_e is the adsorbed phenolic compound quantity per gram of aged-refuse at equilibrium, C_e is unadsorbed phenolic compounds concentration in solution at equilibrium. K and $1/n$ are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. The values of K and $1/n$ can be obtained from the intercept and slope, respectively, of the linear plot of experimental data of $\ln q_e$ versus $\ln C_e$.

Adsorption equilibrium of all the phenolic compounds was modeled using Freundlich isotherms. The initial concentration

Table 5
Dissolvability, partition efficient and dissociation constant of phenolic compounds

	Dissolvability (mg/l)	K_{ow}	pK_a
Phenol	93000	1.46	10.02
2-Chlorophenol	28500	2.17	8.52
4-Chlorophenol	27000	2.35	9.41
2,4-Dichlrophenol	4500	2.75	7.85

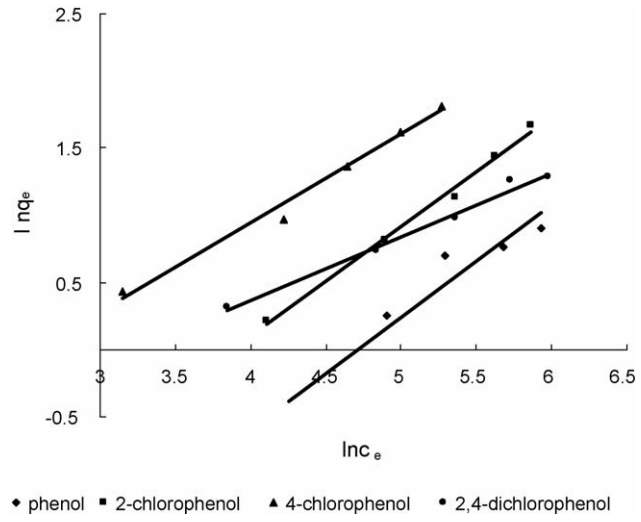

Fig. 6. Freundlich adsorption isotherm.

range from 100 to 500 mg/l. Equilibrium concentration of the tested compounds was plotted to test their fit to the Freundlich equation (Fig. 6). R^2 values, which are a measure of goodness-of-fit, were also calculated from the Freundlich equation. The adsorption isotherms of the test compounds, the Freundlich constants evaluated from the isotherms and the correlation coefficients are given in Table 6.

The equilibrium curves of all the tested compounds are well represented by the Freundlich isotherm model. R^2 values, very close to 1, show that Freundlich isotherm model can adequately describe the adsorption data. As shown in Table 6, the order of the K indicate that the adsorption capacity is 4-chlorophenol, 2,4-dichlorophenol, 2-chlorophenol and phenol. The trend seems to have relation with the polarity of the tested compounds. The electron-withdrawing property of the chlorinated phenol favors the formation of electron donor–acceptor complexes between the aromatic and the active function group in the biomass or the humic substances in the aged-refuse. In addition, the position of the –Cl in the aromatic ring also exerts a greater influence in the adsorption capacity of the aged-refuse. The reason that the adsorption capacity of 4-chlorophenol was greater than 2-chlorophenol, may be result of a steric hindrance of 2-chlorophenol between the –Cl group and the –OH group [13]. For 2-chlorophenol, an intramolecular hydrogen bonding will be formatted between the chlorine atom substituted at the *ortho*-position and the –OH group and decrease the chance of intermolecular hydrogen bonding ability [14]. So compared with 4-chlorophenol, the adsorption capacity will decrease. It can hypothesis that the formation of intermolecular hydrogen bonds plays an important role in the transfer of phenolic compounds from water to the aged-refuse during the adsorption process owning to the chemical adsorption. In addition, with the increase of polarity of the chlorinated phenol, K_{ow} increase and hence enhance the partition function of chlorinated phenol in the organic substances of aged-refuse is another reason that the adsorption capacity of chlorinated phenol is higher than that of phenol.

Adsorption capacity usually has a relationship with the physicochemical properties of the organic compounds, such as K_{ow} (octanol–water partition efficient). Serious studies have correlated with the adsorption of organic pollutants on biomass to the K_{ow} and found a positive relation of K_{ow} to q_e. In this study, in order to investigate the possible mathematical relationship, q_e of all the tested compounds, calculated from the Freundlich equation, was plotted with K_{ow}. The correlation between K_{ow} and the q_e (initial concentration is 500 mg/l) was described by equation:

$$q_e = 2.3583K_{ow} - 0.7684 \quad (2)$$

The q_e increases with the K_{ow} increase, i.e. more hydrophobic organic substances tend to results in a higher equilibrium adsorption capacity. While the correlation coefficient ($R^2 = 0.76$) was rather high indicating that partition function mainly describes adsorption of phenolic compounds to the aged-refuse and the adsorption process is more complex than partition function. If partition function is the only adsorption mechanism, adsorption capacity will have a close relation with the organic content of the aged-refuse and the adsorption isotherm will be linear. But all the value of n is not close to 1 indicating that linear adsorption isotherm dose not exists and the partition function is not the only adsorption mechanism. Based on the trend of the phenolic compound's K_{ow}, if the partition function is the only adsorption mechanism, the trend of the adsorption capacity should be 2,4-dichlorophenol, 4-chlorophenol, 2-chlorophenol and phenol, while the result from the adsorption experiment show that the adsorption capacity of 4-chlorophenol is higher than that of 2,4-dichlorophenol. The values of n, bigger than one, indicate that the interaction between the phenolic compounds and the aged-refuse is strong and the tested compounds can be adsorbed greatly at the low concentration. Based on the data, we can hypothesize that the adsorption process involves in partition function as well as the chemical adsorption.

3.6. Kinetics of the adsorption process

3.6.1. Kinetic model of phenolic compounds adsorption

Kinetic models have been proposed to elucidate the adsorption mechanism. The mechanism of adsorption depends on the

Table 6
Freundlich isotherm equation and the parameters

	Freundlich equation	K	n	R^2
Phenol	$q = 0.0192c_e^{0.837}$	0.019	1.195	0.9345
2-Chlorophenol	$q = 0.042c_e^{0.814}$	0.042	1.228	0.9929
4-Chlorophenol	$q = 0.195c_e^{0.626}$	0.195	1.597	0.9517
2,4-Dichlorophenol	$q = 0.180c_e^{0.662}$	0.180	1.509	0.9854

Table 7
The parameter of the mimetic model

	$q_{(e,exp)}$ (mg/g)	First-order kinetic model			Second-order kinetic model		
		k_1 (min^{-1})	$q_{(e,cal)}$ (mg/g)	R^2	k_2 ($g\,mg^{-1}\,min^{-1}$)	$q_{(e,cal)}$ (mg/g)	R^2
Phenol	0.597	0.012	0.984	0.9898	0.0046	0.77	0.9983
2-Chlorophenol	1.266	0.008	0.977	0.9718	0.0671	1.37	0.9962
4-Chlorophenol	1.752	0.016	0.877	0.9928	0.3503	1.86	0.9984
2,4-Dichlorophenol	1.531	0.014	0.596	0.9784	0.6301	1.55	0.9999

physical and chemical characteristics of the adsorbent as well as on the mass transport process. In order to investigate the mechanism of phenolic compounds adsorption on the aged-refuse and examine the potential rate-controlling step, i.e., mass transfer or chemical reaction. The capability of pseudo-first-order and pseudo-second-order kinetic models was examined in this study. Various kinetic models have been used by various workers, the Lagergren's rate equation is the one most widely used for the solute from a liquid solution:

The pseudo-first-order equation [15–17] is:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \quad (3)$$

where the value of q_e is the adsorption capacity at equilibrium, q_t is the adsorption capacity at time t, k_1 is the rate constants of the pseudo-first-order equation.

On the other hand, a pseudo-second-order equation [15–17] based on the adsorption capacity is expressed in the form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

A series of contact time experiments were carried out with constant initial phenol of 100 mg/l. The pseudo-first-order and pseudo-second-order equation, k_1, k_2, correlation coefficients, theoretical and experimental q_e values were compared in Table 7.

As shown in Table 7, the correlation coefficient of pseudo-second-order equation is higher than that of pseudo-first-order and the theoretical q_e values calculated from pseudo-second-order were more close to the experimental q_e values than from pseudo-first-order. It can be conclusion that the pseudo-second-order kinetic model is fit for the adsorption of phenolic compounds on the aged-refuse. It indicates that the chemical adsorption exists in the adsorption process, which may be partly due to the hydrogen-binding between the hydroxyl groups of phenolic compounds and the active functional groups in the aged-refuse, and it may be the rate-limiting step. Further, there are some deviation between the calculated and the experiment values, it indicates that more than one step involve in the adsorption process.

3.6.2. Diffusion model

In order to investigate that if the diffusion is the control step in adsorption process, the intraparticle diffusion model [15–17] was used to study it.

$$q_t = k_d t^{1/2} + C \quad (5)$$

Table 8
The parameter of the intraparticle diffusion model

	Intraparticle diffusion model	R^2
Phenol	$q_t = 0.0319t^{1/2} + 0.041$	0.956
2-Chlorophenol	$q_t = 0.0431t^{1/2} + 0.048$	0.921
4-Chlorophenol	$q_t = 0.035t^{1/2} + 1.1704$	0.833
2,4-Dichlrophenol	$q_t = 0.0153t^{1/2} + 1.225$	0.797

where k_d and C are the rate constants of intraparticle diffusion (mg/g $min^{1/2}$) and a constants, respectively. The applicability of the model can be examined by plot of q_t, the amount of adsorbate adsorbed per unit weight of adsorbent, versus square root of time. In order to quantify the applicability of the model, the correlation coefficient was calculated from the plot as shown in Table 8.

The higher coefficient (>0.79) shows that the intraparticle diffusion was involved in the adsorption process. The linear portion of the plot does not pass through the origin also indicate that more than one step involve in the adsorption process. The coefficient is lower than that of the pseudo-second-order model suggest that pseudo-second-order adsorption mechanism is predominant and the overall rate of the adsorption process appears to be controlled by the chemical reaction.

3.6.3. Thermodynamics

In order to investigate the thermodynamics characteristics of the phenolic compounds adsorbed by the aged-refuse, adsorption thermodynamics experiment of 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol were conducted at 25, 35 and 45 °C.

The enthalpy change ΔH° and entropy change ΔS° for adsorption are assumed to be temperature independent and the Gibbs free energy ΔG° is related to the enthalpy and entropy by

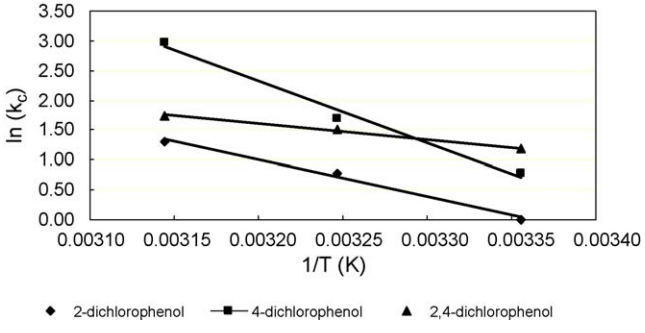

Fig. 7. Plot ln K_C vs. 1/T.

Table 9
The parameter of the thermodynamic

	ΔG° (kJ mol^{-1})			ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1})
	25 °C	35 °C	45 °C		
2-Chlorophenol	−0.281	−1.993	−3.450	5.11	171.6
4-Chlorophenol	−1.904	−4.346	−6.763	8.70	297.9
2,4-Dichlorophenol	−2.924	−3.882	−4.586	2.18	83.3

the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (6)$$

The Gibbs free energy change of the adsorption process can be related to the equilibrium constant by the following equation:

$$\Delta G^\circ = -RT \ln K_C \quad (7)$$

$$\ln K_C = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (8)$$

K_C can be calculated according to the following equation:

$$K_C = \frac{C_A}{C_e} \quad (9)$$

where K_C is the equilibrium constant, C_A is the equilibrium amount adsorbed on the adsorbent per liter of the solution, and C_e is the equilibrium concentration in the solution. T is the solution temperature and R is the gas constant. ΔH° and ΔS° were calculated from the slope and intercept by plotting of $\ln K_C$ versus $1/T$. The relationship between $\ln K_C$ and T is given in Fig. 7 and the estimated adsorption thermodynamic parameters are shown in Table 9.

The positive value of ΔH° conforms that the adsorption process is endothermic, which is an indication of the existence of an interaction between the phenolic compound and the aged-refuse surface.

The positive value of ΔS° indicates a decrease in the order of the system at the solid-solution interface during the adsorption of phenolic compounds. The increases of randomness suggest that it is possibility that some structural changes in the phenolic compounds aged-refuse complex.

The positive values of ΔH° and ΔS° suggest that both enthalpy and entropy are responsible for making the ΔG° negative, The negative value of ΔG° indicates that the adsorption of phenolic compounds on the aged-refuse is spontaneous for the temperature range evaluated, which is usually the case for many adsorption system in solution. As shown in Table 9, the ΔG° value decrease with the increase of temperature, which indicates that the spontaneity of the adsorption process was ensured by the increase of the temperature. Compared with 2-chlorophenol and 2,4-dichlorophenol, the increase of temperature influence the ΔG° value of 4-chlorophenol more greatly owning to the high ΔS° value of it.

4. Conclusions

Adsorption of phenolic compounds by aged-refuse in biofilter was characterized. It was observed that the sorption rate is so rapid that it can get the equilibrium in less than 6 h. The adsorption capacity was strongly dependent on the pH value and has relation with the initial concentration. The adsorption data fit the Freundlich isotherm very well and was correlated with the octanol/water partition. Taking into account the results obtained from experiment sorption, two chemical parameters (K_{ow} and K_a) that seem to play an important role in the sorption process. A comparison of the kinetics models shows that the adsorption process follows pseudo-second-order kinetics. The adsorption process is so complex that more than one step involves in the adsorption process and the overall rate of the adsorption process appears to be controlled by the chemical reaction. The negative values of the Gibbs free energy change of the adsorption indicate that the adsorption is spontaneous. The positive values of the enthalpy of the adsorption show that the adsorption is an endothermic process.

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