Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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Online publication date: 29 November 2010

To cite this Article Ma, Jian-Wei , Wang, Hui , Wang, Fa-Yuan and Huang, Zheng-Hong(2010) 'Adsorption of 2,4-dichlorophenol from Aqueous Solution by a New Low-Cost Adsorbent - Activated Bamboo Charcoal', Separation Science and Technology, 45: 16, 2329 — 2336

To link to this Article: DOI: 10.1080/01496395.2010.504482
URL: http://dx.doi.org/10.1080/01496395.2010.504482

Separation Science and Technology, 45: 2329–2336, 2010

ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496395.2010.504482

Adsorption of 2,4-dichlorophenol from Aqueous Solution by a New Low-Cost Adsorbent – Activated Bamboo Charcoal

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Adsorption experiments were conducted to study the removal of 2,4-dichlorophenol (2,4-DCP) from aqueous solution by a new low-cost adsorbent-activated bamboo charcoal. The results showed that acidic pH was favorable for the adsorption and removal of 2,4-DCP. Higher initial 2,4-DCP concentrations led to higher adsorption capacity. Most of the adsorption of 2,4-DCP occurred within the first 5 min, and about 90% of 2,4-DCP were removed from solution. After 5 min, the adsorption capacity increased slowly with contact time and the adsorption reached equilibrium in less than 100 min. As the adsorbent dose was increased, the removal of 2,4-DCP was increased, while the equilibrium time was slightly affected. Adsorption kinetics could be best described by the pseudo-second-order model, independent of adsorbent dosages. The adsorption behavior of 2,4-DCP onto bamboo charcoal fitted both Langmuir and Freundlich isotherms well, but followed Freundlich isotherm more precisely. This study demonstrated for the first time that activated bamboo charcoal could be used for the removal of 2,4-DCP in water treatment.

Keywords adsorbent; charcoal; isotherm; kinetics; water treatment

INTRODUCTION

Large amounts of contaminants get introduced to ground water and surface water, as well as drinking water, by means of various agricultural and industrial activities, and posed serious ecological and health risks. Considerable efforts have been promoted to develop clean-up techniques for the removal of contaminants from aqueous environments. Adsorption techniques are widely used for water treatment (1). Although commercial activated carbon is a preferred adsorbent, its widespread use is restricted due to the high cost. As such, alternative non-conventional low-cost adsorbents have been investigated and natural, industrial, as well as synthetic materials have been tested for the removal of organics, heavy metals, anions, dyes, etc, from water (2–6).

Bamboo charcoal is produced from the rapidly growing moso bamboo plants, which are distributed widely in China. Currently, the area of bamboo forests is 4.84 million hm^2 in China. The annual growth of bamboo area averages 126 000 hm^2, according to the statistics of the Sixth National Forest Resources Survey (7). The bamboo charcoal is low cost, and its price is only about 1/3 to 1/5 of that of activated carbon in China. It has been applied for many roles in various fields, such as for supplying negative ions, to emit far-infrared rays, to prevent oxidation, to remove microbes from water, as a humidity regulator, and a rich source of minerals, in China, Japan, and Korea (8). Bamboo charcoal burnt at high temperatures (over 800°C) is characterized by a high density, a porous structure, and a huge specific surface area (8). Its adsorption capacity has attracted more attention in recent years (9,10). Several studies have found that bamboo charcoal has excellent adsorption capacity for a wide variety of substances, such as nitrate-nitrogen (11), heavy metals (7,12), dibenzothiophene (13), harmful gases (10,14,15), and can be used for the purification of water or air. Therefore, as a new, innovative, and cost-effective adsorbent, bamboo charcoal may provide an alternative option and deserve more attention.

Chlorophenols represent one of the toxicologically problematic groups. They are generally used as wood preservatives, pesticides, and precursors of herbicides. Chlorophenols are present in drinking water as a result of the chlorination of phenols during disinfection, as by-products of the reaction of hypochlorite with phenolic acids, as biocides, or as degradation products of phenoxy herbicides. Owing to their carcinogenicity and considerable persistence, five of the chlorophenols (2-chlorophenol; 2,4-dichlorophenol; 2,4,6-trichlorophenol; 4-chloro-3-methylphenol and pentachlorophenol) have been classified as

Received 4 October 2009; accepted 29 April 2010.
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priority pollutants by the US EPA (16). According to U.S. National Drinking Water Standards and Health Criteria, the drinking water equivalent level of 2,4-DCP is $100\,\mu g\,L^{-1}$. Numerous studies have found that 2,4-DCP can be adsorbed and easily removed by activated carbon, activated carbon fibers, or other adsorbents (17–21), but no studies have been focused on bamboo charcoal.

In this experiment, the adsorption characteristics of 2,4-DCP onto activated bamboo charcoal were investigated under varying experimental conditions, such as solution pH, initial adsorbate concentration, adsorbent dosage, and contact time. The kinetic and equilibrium data for the adsorption studies were processed to understand the adsorption mechanism of 2,4-DCP onto activated bamboo charcoal.

MATERIALS AND METHODS

Activated Bamboo Charcoal

Activated bamboo charcoal was provided by the Department of Material Science and Engineering, Tsinghua University. Dried strips of moso bamboo (*Phyllostachys heterocycla*) were carbonized in a nitrogen atmosphere at 850°C for 2 h and then cooled naturally to room temperature. After cooling, the carbonized materials were activated by steam at 850°C for 2 h. Before use, activated bamboo charcoal was boiled in distilled water for 1 h to remove some ash and impurities, and then oven-dried at 105°C for 24 h. Then they were ground and passed through 200 mesh (i.e., 0.074 mm) and stored in desiccators. The BET surface area is $1\ 120\,m^2\,g^{-1}$ and the bulk volume is $0.538\,cm^3\,g^{-1}$.

Adsorption Procedure

The reagents used for the analysis are of analytical reagent grade. Standard solutions of 2,4-DCP in distilled water were prepared at $100\,mg\,L^{-1}$ concentrations on the basis of weight by weight (w/w). Three adsorption experiments were carried out in 250 mL conical flasks at room temperature (25°C). The first experiment was to study the effect of adsorbate solution pH. The pH values of adsorbate solutions were adjusted to 2.0, 3.0, 4.0, 6.0, 8.0, 10.0, and 12.0 respectively with HCl or NaOH solutions. Then 100 mL adsorbate solution ($100\,mg\,L^{-1}$) and 0.5 g bamboo charcoal were added into the flasks and then agitated for 6 h at 120 rpm. Solution samples were taken with a syringe after 480 min agitation and treated for analysis. The second experiment was to study the effect of initial adsorbate concentration. Solutions of 2,4-DCP at different concentrations of 0.5, 5, 50, and $100\,mg\,L^{-1}$ were prepared and then treated as the procedure in the first experiment. The third experiment was to study the effect of adsorbent dosage and contact time. Bamboo charcoal at different doses, i.e., 0.2, 0.5, and 1.0 g, respectively, were added into the flasks with 100 mL of adsorbate solution ($100\,mg\,L^{-1}$), and then agitated for 6 h at 120 rpm. Solution samples were taken at 5, 10, 20, 30, 60, 90, 180, 270, 360, and 480 min, respectively. All solution samples were filtered through a 0.45 μm filter membrane for analysis.

Analytical Methods

Solutions of 2,4-DCP were analyzed on a high performance liquid chromatograph (HPLC, Hewlett Packard 1050) at 284 nm equipped with a reverse-phase C18 column (Agilent, USA) and a mobile phase containing methanol and 5% acetic acid solution (67/33, v/v). HPLC was calibrated using four external standards prior to performing chemical analysis and using standard 2,4-DCP during analysis to ensure that the system retained good performance and to certify a consistent response. In addition, the syringe for sample injection was rinsed three times between each injection to eliminate cross-contamination.

Calculation of Adsorption Kinetics and Equilibrium

The amount of adsorbate adsorbed per unit mass of adsorbent at time t (q_t, $mg\,g^{-1}$), and the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium, (q_e, $mg\,g^{-1}$), were calculated from the following equations:

$$q_t = V \times \frac{C_0 - C_t}{m_s} \tag{1}$$

$$q_e = V \times \frac{C_0 - C_e}{m_s} \tag{2}$$

where C_0 and C_e ($mg\,L^{-1}$) are the initial and the final concentrations of adsorbates in flasks, respectively, C_t ($mg\,L^{-1}$) is the concentrations of adsorbates at time t. V is the volume of the solution (L) and m_s is the mass of dry adsorbent used (g).

RESULTS AND DISCUSSION

Effect of Adsorbate Solution pH

Some adsorbents may have affinity for H^+ or OH^- ions and can directly affect the solution pH, causing changes in the solubility and adsorption capacity. Also, the H^+ and OH^- ions affect the adsorption process through dissociation of the functional groups on the adsorbate and adsorbent (22). It has been suggested that phenol and its derivatives adsorption on activated carbon via a "donor–acceptor complex" mechanism that involves carbonyl surface- oxygen groups acting as electron donor, and the aromatic ring of the solute acting as acceptor (23). On the surface of activated bamboo charcoal, many oxygen-containing functional groups, such as carbonyl, carboxyl, hydroxyl, and formylphenyl, may play negative or positive roles in adsorption. Adsorbate solution pH can change their chemical properties, thus further influencing the adsorption process. Therefore, the pH of the adsorption

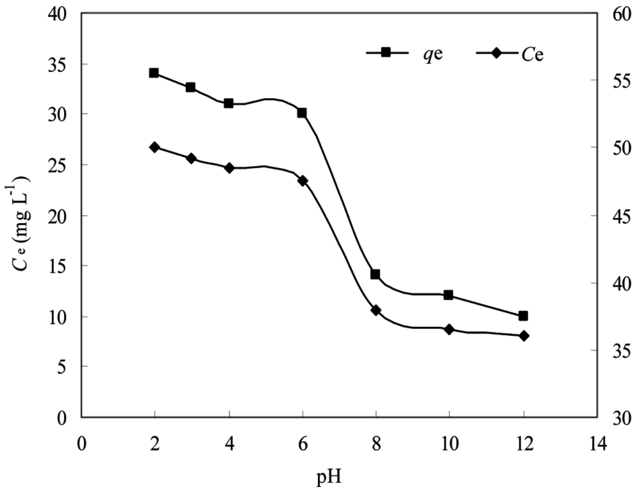


FIG. 1. Effect of solution pH on residual concentrations (C_e) of 2,4-DCP and adsorption capacity (q_e) of bamboo charcoal for 2,4-DCP.

medium is the most significant parameter in the adsorption of chlorophenols (24).

Figure 1 showed the effect of the initial solution pH on adsorption characteristics of 2,4-DCP onto bamboo charcoal. When initial pH of the 2,4-DCP solution increased from 2 to 12, the residual concentrations of 2,4-DCP (C_e) increased from 10 to 34 mg L^{-1}(Fig. 1). Similar results were reported for 2,4-DCP adsorption by coir pith carbon or calm pith carbon (3,20). The adsorption capacity of bamboo charcoal (q_e) also decreased from 50 to 36 mg g^{-1} (Fig. 1). A sudden change occurred from pH 6 to 8. The pKa value of 2,4-DCP is 7.85 ($C_6H_3Cl_2OH \rightarrow C_6H_3Cl_2O^- + H^+$, pKa = 7.85). At acidic pH values, 2,4-DCP mainly exists in the non-dissociated forms, and the adsorbent surface carries a positive charge, thus there is no electrostatic repulsion between the adsorbate and the adsorbent, leading to easy adsorption onto bamboo charcoal. When pH increases, more 2,4-DCP molecules dissociate into $C_6H_3Cl_2O^-$, and the number of negatively charged surface functional groups also increases. For example, the −COOH groups present in the bamboo charcoal are converted into $-COO^-$. The electrostatic repulsion between the identical charges lowers the adsorption capacities. In another way, the anions are more soluble in the aqueous solution, and stronger adsorbate-water bonds must be broken before adsorption can take place. Besides, OH^- ions compete with 2,4-DCP molecules or $C_6H_3Cl_2O^-$ in occupying the adsorption sites. These may explain the lower removal percentages of 2,4-DCP and smaller adsorption capacity of bamboo charcoal at higher pH.

Effect of Initial 2,4-DCP Concentration

It is generally accepted that the adsorption capacity of adsorbents is larger when the adsorbate has a high

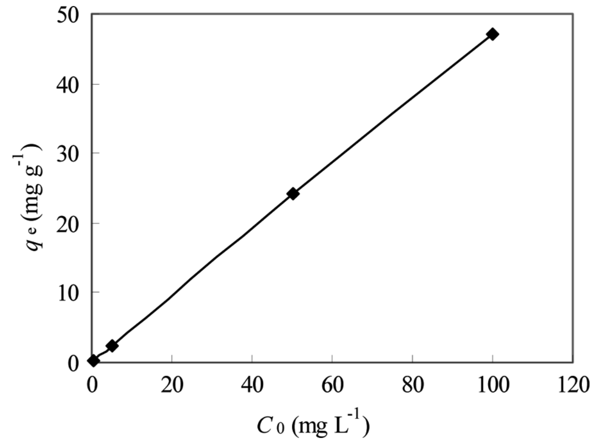


FIG. 2. Effect of initial 2,4-DCP concentration (C_0) on adsorption capacity (q_e) of bamboo charcoal for 2,4-DCP.

concentration or a smaller solubility in water. The effect of 2,4-DCP concentration on the adsorption by bamboo charcoal was investigated with 2,4-DCP solutions at different initial concentrations (0.5, 5, 50, and 100 mg L^{-1}). Figure 2 showed that the initial 2,4-DCP concentrations in the experiment had a positive correlation with q_e. The reasons may be similar to those at different adsorbent doses. When the initial concentration was low, the surface area and the availability of adsorption sites were relatively high, thus more 2,4-DCP was removed but q_e was decreased.

Effect of Adsorbent Dosage on Adsorption Kinetics

Adsorption characteristics of 2,4-DCP by bamboo charcoal varied with contact time (Fig. 3). Most of the adsorption of 2,4-DCP occurred within the first 5 min, and about 90% of 2,4-DCP were removed from solution

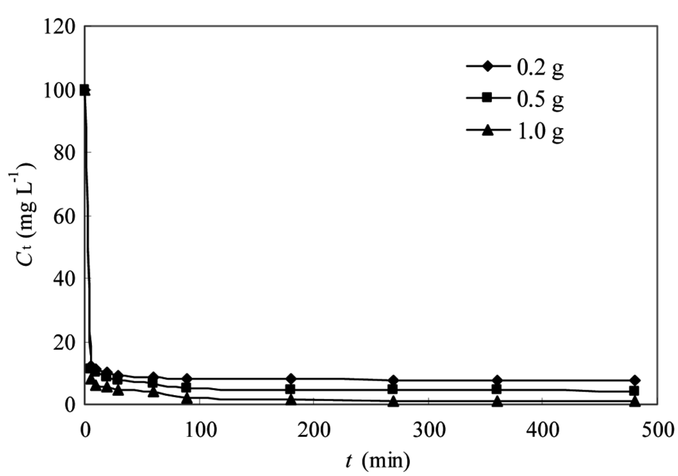


FIG. 3. Effect of adsorbent dosage and contact time on adsorption of 2,4-DCP by bamboo charcoal.

under different doses of bamboo charcoal. After 5 min, the adsorption capacity increased slowly with the contact time. This is simply due to the reduction of driving force after a longer period of operation. At adsorption equilibrium, 95.50%, 97.84%, and 99.48% of 2,4-DCP was removed at 0.2, 0.5, and 1.0 g doses of bamboo charcoal respectively. Clearly, increase in adsorption with the adsorbent dosage can be attributed to increased surface area and the availability of more adsorption sites.

At 0.2, 0.5, and 1.0 g doses of bamboo charcoal, q_t at 5 min was 42.15, 18.07, and 9.34 mg g^{-1}, respectively, while q_e was 46.72, 19.86, and 10.10 mg g^{-1} respectively. This was probably due to unsaturated adsorption at the higher dosage of adsorbent, and/or aggregation of adsorption sites resulting in decrease in the total adsorbent surface area available to 2,4-DCP and an increase in the diffusion path length.

Generally, equilibrium time was lesser at higher adsorbent doses (25). However, our results showed that the dose of adsorbents had a slight effect on equilibrium time of adsorption, and the adsorption reached equilibrium in less than 100 min, independent of adsorbent doses. This may be attributed to the fact that all the doses of bamboo charcoal, even the lowest dose, can provide enough adsorption sites and contact 2,4-DCP quickly. When the amount of 2,4-DCP is larger, the effect of adsorbent dosage on equilibrium time may appear significantly.

Kinetic data were used for assigning the appropriate models for explaining the nature of adsorption process. The pseudo-second-order equation developed by Ho and McKay (26) was adopted in this study. The pseudo-second-order equation is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where q_e and q_t are the amount of 2,4-DCP adsorbed (mg g^{-1}) at equilibrium and at time "t", respectively, and k_2 is the equilibrium rate constant of the pseudo-second-order chemical adsorption (g mg^{-1} min). Kinetic parameters were calculated from the slope and intercept of the linear plots of t/q_t versus t (Table 1). The linear plots of t/q_t versus t (Fig. 4) show a good agreement between experimental

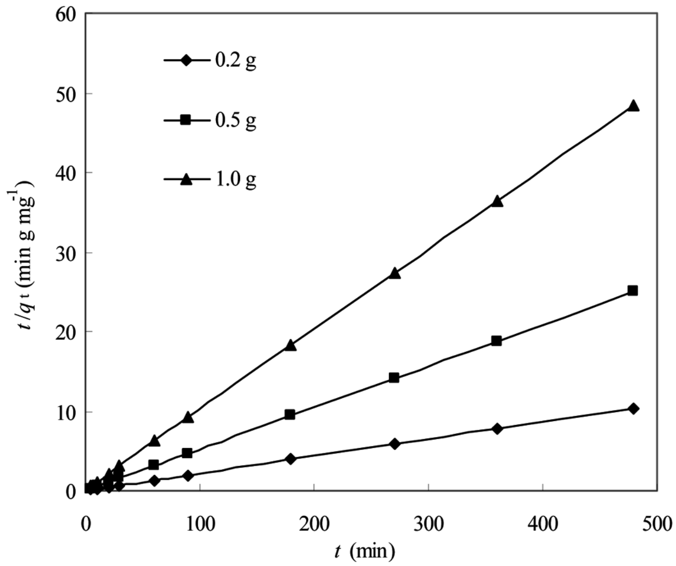


FIG. 4. Pseudo-second-order kinetic plots for the adsorption of 2,4-DCP onto bamboo charcoal at different dosages.

and calculated q_e values (Table 1). The correlation coefficients (R) for the second-order kinetic model were 1 or 0.999, indicating the highest applicability of this kinetic equation and the second-order nature of the adsorption of 2,4-DCP by bamboo charcoal. As the adsorbent dosage increased, the values of k_2 increased while q_e significantly decreased.

The error squares (SE, %) are also calculated according to the following equation:

$$\mathrm{SE}(\%) = \sqrt{\frac{(q_{e,exp} - q_{e,cal})^2}{N}} \tag{4}$$

where N is the number of data points, $q_{e,exp}$ and $q_{e,cal}$ are the amounts of the adsorbed 2,4-DCP measured and calculated at equilibrium (mg g^{-1}), respectively. The lower the value of SE (Table 1) and the higher the value of R, the better is the fitness of the model. It can be concluded that the adsorption kinetics of 2,4-DCP onto bamboo charcoal can be best described by the second-order model, independent of adsorbent dosages.

TABLE 1
Kinetic parameters for the adsorption of 2,4-DCP onto bamboo charcoal at different dosages

Adsorbent dose (g)	$q_{e,cal}$	k_2 (g mg^{-1} min)	R	SE (%)
0.2	46.30	0.036	1	0.133
0.5	19.19	0.051	0.999	0.212
1.0	9.93	0.089	1	0.054

Adsorption Isotherms

The adsorption isotherms represent the relationship between the amount adsorbed by a unit weight of adsorbent and the amount of adsorbate remaining in the solution at equilibrium. Two well known isotherms, Langmuir and Freundlich, have been shown to be suitable for describing short-term and mono-component adsorption. The Freundlich isotherm model assumes heterogeneous surface energies, in which the energy term in Langmuir equation varies as a function of the surface coverage (27). The Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface (27). The applicability of the isotherm equation is compared by judging the correlation coefficients, R^2.

Freundlich Isotherm

The Freundlich model is given by the following equations.

Exponential form:

$$q_e = K_f C_e^{1/n} \tag{5}$$

Logarithmic form:

$$\lg q_e = \lg K_f + \frac{1}{n} \lg C_e \tag{6}$$

where C_e is the equilibrium concentration of 2,4-DCP ($mg\,L^{-1}$), q_e is the adsorption amount of 2,4-DCP at equilibrium ($mg\,g^{-1}$), K_f ($L\,g^{-1}$) and n are the Freundlich constants which show the adsorption capacity of the adsorbent and the affinity between the adsorbent and adsorbate. The plot of lg q_e versus lg C_e showed a straight line with slope '$1/n$' (Fig. 5a), indicating that the adsorption of 2,4-DCP follows the Freundlich isotherm.

The Freundlich constants (K_f and $1/n$) were calculated and recorded in Table 2. The slope $1/n$, ranging between 0 and 1, is a measure of adsorption intensity or surface heterogeneity. A value for $1/n$ below one indicates a normal Langmuir isotherm while $1/n$ above one is indicative for a cooperative adsorption. The other Freundlich constant K_f indicates the adsorption capacity of the adsorbent. The value of K_f at equilibrium was 20.48 (Table 2), indicating a greater affinity between 2,4-DCP and bamboo charcoal.

Langmuir Isotherm

The linear form of Langmuir's isotherm model is given by the following equation:

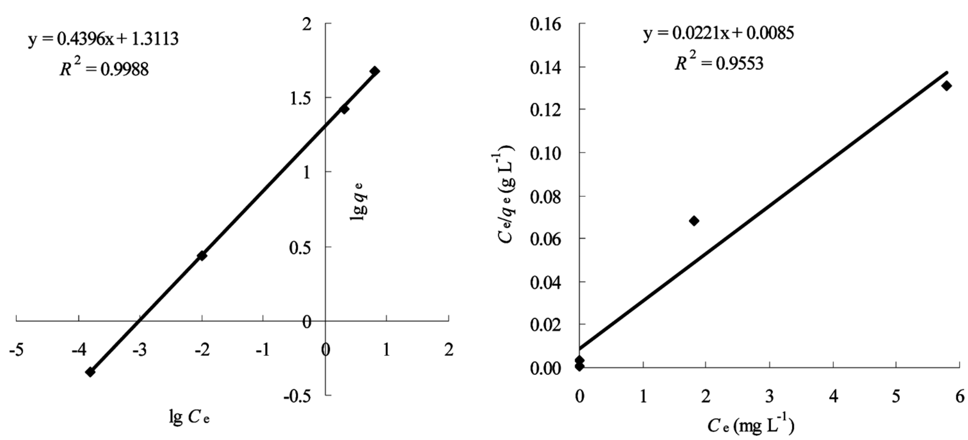
$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \tag{7}$$

where C_e is the equilibrium concentration of 2,4-DCP ($mg\,L^{-1}$), q_e and q_m are the equilibrium amount and maximum amount of 2,4-DCP adsorbed per unit mass of adsorbate ($mg\,g^{-1}$), respectively, and b is the Langmuir constant related to the rate of adsorption. When C_e/q_e was plotted against C_e a straight line with slope $1/q_m$ was obtained (Fig. 5b), indicating that the adsorption of 2,4-DCP on bamboo charcoal also follows the Langmuir isotherm. The Langmuir constants b and q_m were calculated from this isotherm and their values are given in Table 2.

The effect of the isotherm shape has been discussed (28) with a view to predict whether an adsorption system is favorable or unfavorable. The essential feature of the Langmuir isotherm can be expressed by means of 'R_L', a dimensionless constant referred to as the separation factor or the equilibrium parameter. R_L is calculated using the following equation:

$$R_L = 1/(1 + bC_0) \tag{8}$$

where C_0 is the initial 2,4-DCP concentration ($mg\,L^{-1}$). The value of R_L indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). Values of R_L were shown in Fig. 6, which confirmed that the bamboo



(a) (b)

FIG. 5. Freundlich (a) and Langmiur (b) adsorption isotherms of 2,4-DCP onto bamboo charcoal.

TABLE 2
Langmuir and Freundlich constants for 2,4-DCP adsorption by various low-cost adsorbents in this work and other literatures

Adsorbent	q_m (mg g^{-1})	b(L mg^{-1})	K_f (L g^{-1})	n	Reference
Activated bamboo charcoal	45.25	2.60	20.48	2.27	This work
Apricot stone shell (AP-42)	339	0.197	43.65	1.50	(29)
Coir pith carbon	19.12	0.72	2.45	1.21	(30)
Paper mill sludge	4.49	0.003	–	–	(31)
Fly ash	*	*	7.20	86.96	(32)
Activated sludge biomass	*	*	0.37–0.94	0.72–0.90	(33)
Palm pith carbon	19.16	0.706	5.895	1.901	(20)
Immobilized *Phanerochaete chrysosporium*	7.15	0.039	0.52	1.75	(34)
Phanerochaete chrysosporium biomass	11.62	0.0147	0232	1.256	(35)
Blast furnace sludge	38.6	*	–	–	(36)
Blast furnace dust	29.1	*	–	–	(36)
Pomegranate peel	75.8	0.042	–	–	(37)
Fly ash	22.17	*	–	–	(38)
Aged-refuse in biofilter	1.531	*	0.18	1.509	(39)
Coal fly ash	1.81–4.36	*	–	–	(40)
Maize cob	17.94	0.907	–	–	(41)
Silk cotton hull	16.0	0.3341	4.466	2.252	(42)
Oil palm empty fruit bunches	27.25	0.56	3.42	2.00	(43)
Jackfruit peel	400.0	0.0024	9.00	1.96	(44)

*Indicates adsorption does not follow Langmuir isotherm; – indicates adsorption does not follow Freundlich isotherm.

charcoal is favorable for adsorption of 2,4-DCP under conditions used in this study.

Numerous studies have found that the adsorption process of phenols and chlorophenols (including 2,4-DCP) can be best-fitted by the Freundlich isotherm (see Table 2). The linear isotherm and the Freundlich isotherm fit well the adsorption of 2,4-DCP by marine sediments,

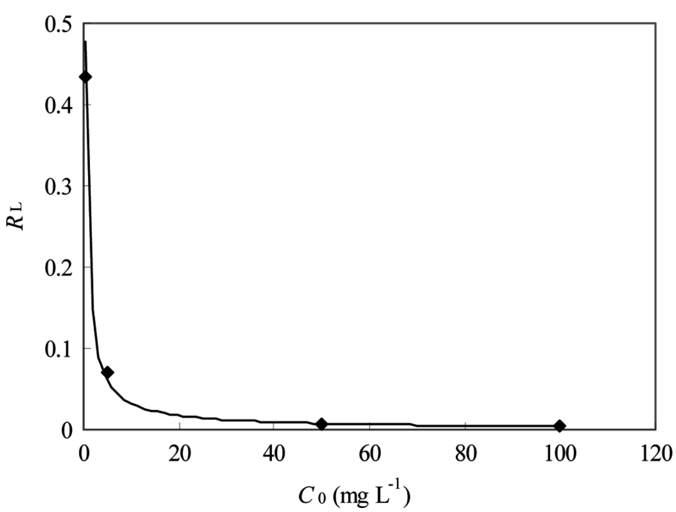


FIG. 6. Plot of R_L against initial 2,4-DCP concentration.

but the Langmuir isotherm fit is poor (27). Our results were in agreement with these studies. As seen from Fig. 5, the Freundlich isotherm fitted more precisely ($R^2 = 0.9988$) than the Langmuir isotherm ($R^2 = 0.9553$).

Here, we first reported the excellent adsorption of activated bamboo charcoal for 2,4-DCP. The adsorption capacity of different low-cost adsorbents used for 2,4-DCP removal was compared and it was found that the activated bamboo charcoal had a higher adsorption capacity than most of the others (Table 2). As an inexpensive, indigenous, and easily available adsorbent, activated bamboo charcoal may be effective for the removal of 2,4-DCP from water.

Adsorption mechanisms of 2,4-DCP by bamboo charcoal may be diverse. It is known that −Cl groups are strong electron-withdrawing groups in reducing the overall electron density in the π-system of the ring enhancing attraction with the surface of carbon (17,18). Thus, high adsorption capacities were observed for chlorinated phenols. On the other hand, the adsorption capacity closely correlates with the variation of the surface area and porosity of the adsorbent. Higher surface area and pore volume would result in higher adsorption capacity. Carboxyl and hydroxyl groups inhibited the adsorption of phenols by activated carbon and increased the affinity of the carbon towards water, and, therefore, the solvent molecules could effectively block some micropores, while carbonyl groups enhance adsorption (29). The adsorption capacity of phenols on granular activated carbon is affected by hydrogen-bonding between adsorbates and adsorbents (23). In our experiment, a number of oxygen-containing functional groups exist in bamboo charcoal surface after activation, including electron acceptors (e.g., carbonyl and carboxyl) and electron donors (e.g., hydroxyl). It is hence probable to form hydrogen bonds between the electron-acceptor groups on the activated bamboo charcoal surface and the hydrogen atoms on 2,4-DCP. Obviously, adsorption mechanisms of 2,4-DCP onto bamboo charcoal still need a detailed study. Additionally, adsorption and removal of more organic pollutants using bamboo charcoal deserve more attention in future water treatment applications.

CONCLUSIONS

Adsorption studies were performed on activated bamboo charcoal to remove 2,4-DCP from aqueous solution. The results showed that at lower pH values, more 2,4-DCP was adsorbed and removed. Higher initial 2,4-DCP concentrations led to higher unit adsorption capacity. Most of the adsorption of 2,4-DCP occurred within the first 5 min, and about 90% of 2,4-DCP were removed from solution under different doses of bamboo charcoal. After 5 min, the adsorption capacity increased slowly with contact time and the adsorption reached equilibrium in less than 100 min. As the adsorbent dose was increased, the removal of 2,4-DCP adsorbed increased, while the equilibrium time was slightly affected. Regardless of the adsorbent dosages, the adsorption kinetics of 2,4-DCP onto bamboo charcoal could be best described by the pseudo-second-order model. Adsorption of 2,4-DCP onto bamboo charcoal fitted both the Langmuir and Freundlich isotherms well, but followed the Freundlich isotherm more precisely. As an inexpensive, indigenous, and easily available adsorbent, activated bamboo charcoal shows a potential for the removal of 2,4-DCP from aqueous solution.

ACKNOWLEDGEMENTS

This work was supported by the Water Pollution Control and Management Project of China (2008ZX07313-001, 2008ZX07313-003) and by the National Key Technologies R&D Program of China (2007BAC22B02).

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