Removal of endocrine disrupting chemicals from aqueous phase using spherical microporous carbon prepared from waste polymeric exchanger

Chao Long, Jundong Lu, Aimin Li and Quanxing Zhang

ABSTRACT

A spherical microporous carbon adsorbent (CR-1), which was developed by carbonization and activation of the waste polysulfonated cation-exchanger, was used to remove Dimethyl phthalate (DMP) and 2, 4-dichlorophenol (2, 4-DCP) as the model compounds of EDCs from the aqueous solution. Four adsorption isotherm models, Langmuir, Freundlich, Toth and Polanyi–Dubinin–Manes isotherms models provided the best correlation. The Henry’s law constants calculated from Toth equation were found to be 705.957 and 6,724.713 L g$^{-1}$ for 2, 4-DCP and DMP at 298 K, respectively, and the larger exponents n of the Freundlich model were 9.011 and 9.93 for 2, 4-DCP and DMP at 298 K, respectively. The values of Henry’s law constants and exponent n of the Freundlich suggested that CR-1 was an effective adsorbent for removal of low concentrations of DMP and 2, 4-DCP from aqueous solution. Moreover, the adsorption kinetics results showed that adsorption of 2, 4-DCP and DMP on CR-1 was a pseudo-second-order process controlled by intra-particle diffusion and that adsorption uptake reached quickly half of equilibrium capacities within 20 min.

Key words | adsorption, 2, 4-dichlorophenol, dimethyl phthalate, waste ion exchange resin

INTRODUCTION

Recently, endocrine disrupting chemicals (EDCs) have become a focus of significant attention as a class of environmental contaminants. Many researchers have reported that EDCs may promote chromosome injuries in human leucocytes and interfere with the reproductive system and normal development of animals and humans. Among the EDCs, phthalate and phenolic compounds have been widely detected in the environment and effluents of wastewater treatment plants due to their wide applications in various industrial production processes. To remove phthalate esters and phenolic compounds from water and wastewater intended for direct or indirect reuse, an advanced treatment process should be applied. Among the range of possible treatment technologies, activated carbons adsorption has been shown to be an effective treatment for removing phthalate esters and phenolic compounds from aqueous solutions (EPA 2001; Adhoum & Monser 2002; Ayranci & Bayram 2005; Choi et al. 2005). However, owing to the high production costs of common activated carbons and insufficient supply, recently there has been noticed a growing interest for the production of low-cost adsorbents from agricultural and industrial by-products (Daifullah & Girgis 1998; Galiatsatou et al. 2001; Gupta et al. 2004; Singh et al. 2008).
Polymeric ion-exchange resins are used mainly for demineralization of boiler water and metal separation from aqueous solutions. Generally, they become waste in 3–5 years of their exploitation and are practically undegradable in the environment. In China, the amount of the waste polymeric ion exchange resins is increasing owing to the rapid economic development. Therefore, the effective method to treat and utilize the waste resin is required. Polymeric resins have been found to be suitable precursors for the production of activated carbons because of high carbon yield and low ash content (Lenghaus et al. 2002; Park & Jung 2002). From the practical point of view, the use of waste ion-exchange resins for manufacturing carbon adsorbents may be of a very big economic and ecological advantage. Reports have appeared on the preparation of carbon adsorbents from the waste ion-exchange resins (Horikawa et al. 2002; Bratek et al. 2003; Gun’ko et al. 2005), however, much attention has been paid to the influence of the preparation methods on the porosity and structure of activated carbons. So far, there have been only few papers that investigated the effectiveness of removing contaminants by means of adsorbents obtained from waste ion exchange resins (Bratek et al. 2002).

In the present study, the waste ion exchange resins were utilized as precursors to prepare the spherical microporous carbon adsorbent (CR-1), and dimethyl phthalate and 2, 4-dichlorophenol (2, 4-DCP) were chosen as the model compounds of EDCs to investigate the adsorption characteristics of CR-1. The adsorption data were described by four isotherm models, Langmuir, Freundlich, Toth and Polanyi–Dubinin–Manes equations. In addition, the adsorption kinetics was explored using three kinetic models, pseudo-first-order, pseudo second-order and intra-particle diffusion kinetics models. The aim of our research was to determine the effectiveness of removing dimethyl phthalate and 2, 4-dichlorophenol from aqueous solutions by microporous carbon adsorbent (CR-1).

MATERIALS AND METHODS

Materials

Waste sulfonated Polystyrene-based cation-exchange resins (WER), which had been used for demineralization of boiler water for about two years, were supplied by Jiangsu Yangnong Chemical Industrial Groups. Prior to use, WERs were packed into a column and first treated with 1.0 N HCL and then washed by deionized water until the wash solution had achieved a neutral pH value. Dimethyl phthalate (DMP) and 2, 4-dichlorophenol (2, 4-DCP) were purchased from Sigma-Aldrich Chemical Co. All the reagents were of analytical reagent grade and were used without further purification. DMP) and 2, 4-DCP were dissolved in deionized distilled water without pH adjustment for adsorption experiments.

Preparation of CR-1

WERs were used as the starting material to produce carbon adsorbents by carbonization and subsequent activation. First, WERs were placed in flow quartz reactor, heated up to 450°C at a heating rate of 6°C min⁻¹ in a nitrogen atmosphere, and maintained at the desired activation temperature for 90 min. After the carbonization step, the chars were continuously heated to 850°C at a heating rate of 6°C min⁻¹ in a nitrogen atmosphere. At 850°C, the nitrogen flow was stopped and carbon dioxide was introduced in the meantime. Activation was carried out using carbon dioxide as activator at this temperature for 180 min. Finally, the activated product (CR-1, 0.5–0.8 mm in diameter) was washed sequentially with 0.5 N HCL solutions, and distilled water to remove some of the ash and decomposed fragments and then dried at 110°C for 24 h.

The morphology of CR-1 was examined in an SEM (Hitachi S-4300, Japan). The CR-1 was coated with platinum by a platinum sputtering device for clear visibility of the surface morphology.

N₂ adsorption isotherm of CR-1 at 77 K was measured using an ASAP 2010 (Micromeritics Instrument Co., USA). The BET surface area, micropore pore volume and mesopore pore volume were calculated from the N₂ isotherms data by BET, Dubinin–Astakov (DA) and BJH methods, respectively. The total pore volume was estimated to be the liquid volume of nitrogen at a relative pressure of about 0.95.

Adsorption experiments

Equilibrium adsorption studies of DMP and 2, 4-DCP were performed at 283 K, 298 K and 313 K, respectively. Thus, an
accurately weighted amount of CR-1 and 100 mL solution of DMP and 2, 4-DCP were introduced directly into each of a series of 250 mL conical flasks. The initial concentrations of the aqueous solutions of Dimethyl phthalate and 2, 4-dichlorophenol for adsorption equilibrium experiment were 20, 60, 80, 100, 200, and 300 mg/L, respectively. These flasks were then shaken at 150 rpm in an incubator shaker with thermostat for 48 hr to attain equilibrium. The residual concentration of the aqueous phase, \( C_e \) (mg/L) was determined by high-performance liquid chromatography (HPLC) with diode array detector (Waters Associates, USA) at a wavelength of 240 nm and 270 nm for DMP and 2, 4-DCP, respectively, employing a water/methanol (30:70 v/v) solution as the mobile phase.

Such kinetic experiments were conducted employing the batch method. Thus, 0.4 g dry adsorbent and 400 mL of 100 mg/L of DMP and 2, 4-DCP were introduced into a 500 mL flask, which was then placed in a water bath at 298 K and agitated mechanically at a stirring speed of 120 rpm. At given time intervals, about 0.1 mL of solution was withdrawn from the flask via a syringe and its concentration determined by HPLC methods.

## RESULTS AND DISCUSSION

### Characterization of CR-1

The morphology of CR-1 was observed in a scanning electron microscope (Figure 1). The regular spherical shape of the polymeric resins is preserved after the activation and the surface is quite smooth except for a few occasional cavities. Under high magnification (20,000 times), CR-1 is shown to have a well-developed pore structure. Its textural parameters are listed in Table 1, in which was shown that the micropore volume and micropore surface area account for about 86.8% of the total pore volume and 82.5% of BET surface area, respectively.

### Isotherms study

The equilibrium adsorption isotherms of DMP and 2, 4-DCP from aqueous solution onto CR-1 at different temperatures are depicted in Figure 2(a–d). Favorable adsorption isotherms were exhibited for DMP and 2, 4-DCP with the extent of adsorption increasing as the equilibrium concentration of the adsorbate increased. In order to understand the adsorption mechanism and optimize the design of an adsorption system, the equilibrium adsorption data of DMP and 2, 4-DCP on CR-1 at different temperatures were fitted using the nonlinear isotherm models, i.e. Freundlich (FM), Langmuir (LM), Toth and Polanyi–Dubinin–Manes (PDM) models (Table 2). It is quite obvious from Figure 2(a–d) that Langmuir and Freundlich model represented the poorer fit of experimental data, but PDM and Toth equations, which based on Polanyi potential theory, provided the best correlation for experimental data, supported by the largest \( R^2 \).

The Toth model is derived from potential theory and possesses the correct Henry’s law behavior. It is valuable to evaluate the Henry’s constant because it has been used as a criterion of the adsorption affinity. By using Equation (1) based on Toth model, the larger Henry’s constant was achieved, 705.957 and 6,724.713 Lg\(^{-1}\) for 2, 4-DCP and DMP at 298 K, respectively, which manifested that CR-1 represents an excellent adsorption affinity for 2, 4-DCP and DMP in dilute condition.

\[
H = \lim_{C \to 0} \frac{q}{C} = \lim_{C \to 0} \frac{dq}{dC} = \frac{Q_{\text{max}}}{B/L} \quad (1)
\]

Polanyi–Dubinin–Manes (PDM) model, which is based on theory of Volume Filling of Micropores, has
been successfully applied to describe the adsorption of organics from aqueous solution on micropore solids (Li et al. 2005; Yang et al. 2006). In brief, the theory postulates that adsorption is a process of (micro)pore filling mechanism and that the volume occupied by the adsorbed compound is a temperature-independent function of the adsorption potential($\varepsilon$). A direct consequence of these assumptions is that, for a given sorbent, plots of adsorbed

![Figure 2](image_url) Adsorption isotherms of DMP and 2, 4-DCP onto CR-1 at 283, 298 and 313 K.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Nonlinear isotherm models</th>
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<td>Name</td>
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<tr>
<td>Freundlich model</td>
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<td>Langmuir model</td>
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<td>Toth model</td>
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<td>Polanyi–Dubinin–Manes model</td>
<td>PDM</td>
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$q_e[\text{mmol/g}]$, equilibrium adsorbed capacity; $C_e[\text{mmol/L}]$, equilibrium solution phase concentration; $Q_0[\text{mmol/g}]$, adsorbed capacity; $C_s[\text{mmol/L}]$, aqueous water solubility.
volume $q_e$ against $e$ will form a temperature-independent adsorption “characteristic” curve, which is often employed to examine whether the Polanyi theory mechanically captures the adsorption process. The characteristic curves of each adsorbate are represented in Figure 3. As the Polanyi theory would predict, they all fell essentially onto a single curve for the adsorption of DMP and 2, 4-DCP onto CR-1, respectively. The applicability of the PDM and Toth isotherm models implies that the mechanistic usefulness of Polanyi theory to describe adsorption of DMP and 2, 4-DCP onto CR-1, and the micropore filling is the dominating mechanism for the adsorption of DMP and 2, 4-DCP onto CR-1.

**Adsorption kinetics**

Three kinetic models, including pseudo-first-order, pseudo-second-order, and intra-particle diffusion models, were used to investigate the adsorption process. The pseudo-first-order and pseudo-second-order models expression may be expressed by the following relationships, respectively.

\[
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t
\]\n
\[
\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{t}{q_e}
\]\n
\[
t_{1/2} = \frac{1}{k_2 q_e}
\]

Where $q_e$ and $q_t$ are the amounts of DMP and 2, 4-DCP adsorbed onto the adsorbents at equilibrium and at time $t$, respectively (mmol/g), and $k_1$ is the pseudo-first-order rate constant (min$^{-1}$), $k_2$ is the pseudo-second-order rate constant (g/mmol min), $t_{1/2}$ is the time at which the adsorption capacity $q_t$ reaches half of the equilibrium adsorption capacity $q_e$.

Figure 4 depicts the influence of contact time on the removal of DMP and 2, 4-DCP by CR-1 at 298 K. The calculated kinetic parameters along with correlation coefficients by applying the kinetic models are listed in Table 3. As can be seen from Table 3 and Figure 4, higher correlation coefficients ($R^2 > 0.97$) and more reasonable calculated $q_e$ values close to the experimental data indicated that the pseudo-second-order kinetic model might be suitable to describe the kinetics adsorption process of 2, 4-DCP and DMP onto CR-1. It is also evident that the adsorption uptake of CR-1 for 2, 4-DCP and DMP increased quickly at the initial stage, and the time $t_{1/2}$ of reaching half of equilibrium capacities is 18.97 min and 16.44 min, respectively. This demonstrates the good potential of CR-1 for practical use in the removal of 2, 4-DCP and DMP from the aqueous solution.

For the interpretation of experimental kinetics data from a mechanistic viewpoint, prediction of the rate-limiting step is an important consideration. In general, the adsorbate transported from the solution phase to the pore surface of the adsorbent occurs in several steps: mass transfer from fluid phase to the particle surface across the boundary layer, diffusion within the porous particle (pore diffusion and surface diffusion), and adsorption itself onto the pore surface. The overall adsorption process may be controlled by one or more steps. The rate of intra-particle diffusion is in most cases the rate-determining step in adsorption processes. The most widely applied intra-particle diffusion equation is given by Weber & Morris (1963) as:

\[
q_t = k_d t^{0.5} + c
\]

Where $k_d$ is the intraparticle diffusion rate (mmol/g min$^{-0.5}$), and $c$ is a constant.

If the plot of $q_t$ versus $t^{0.5}$ satisfies the linear relationship with the experimental data, then the adsorption process is found to be controlled by intra-particle diffusion only. However, if the data exhibit multi-linear
plots, then two or more stages influence the adsorption process. Figure 4 indicates that the plot of $q_t$ versus $t^{0.5}$ was multi-linear, and yields a straight line passing through the origin at the initial stage of adsorption. The first sharper portion describes the external surface or macroporous adsorption. The second portion is the gradual adsorption stage, where the intra-particle diffusion is rate-controlled. The third linear portion corresponds to the final equilibrium stage, where the intra-particle diffusion starts to slow down and the equilibrium is established. The $k_d$ values of different stages for the two compounds are shown in Table 3. It is obvious that the order of adsorption rate follows the order $k_1 > k_2 > k_3$ for the two adsorbates.

The results of adsorption kinetics experiments could be explained from the structure of absorbents. The CR-1, from the Table 1, is found to be microporous adsorbent contains a proportion of mesopores. Therefore, the first portion of plot of $q_t$ versus $t^{0.5}$ in Figure 4 is attributed to the diffusion of adsorbate through the solution to the external surface and macropore of adsorbent, and the second straight portion depicting mesopore diffusion and the third representing micropore diffusion. Previous studies (Guo et al. 2003; Valderrama et al. 2008) also showed that such multi-linearity plots might present a confirming that the different stages of intra-particle diffusion in the macro-, meso-, and micropores structure of the adsorbent.

### Evaluation of CR-1 as an adsorbent for DMP and 2, 4-DCP

Comparisons between the adsorption results of 2, 4-DCP and DMP in this work and those in other relevant studies are summarized in Table 4. In this study, the values of $Q_0$ in the Langmuir model, which is an indicator of adsorption capacity, and $n$ in Freundlich model, which is an indicator of adsorption intensity, were compared to those in most of

![](https://iwaponline.com/wst/article-pdf/60/6/1607/447536/1607.pdf)
other relevant studies. As shown in Table 4, the CR-1 had the largest values of adsorption capacities \( (Q_0) \) and adsorption intensities \( (n) \) for 2, 4-DCP as compared to those of carbons derived from by-products (no available adsorption data of carbons derived from by-products for DMP in references); compared with conventional activated carbon and polymeric adsorbents, through the adsorption capacities of CR-1 for DMP and 2, 4-DCP were the lowest, n values were the largest. The experimental results above demonstrated that the microporous carbon prepared from waste ion exchange resin was a potential cost-effective adsorbent for removal of EDCs in water/wastewater, especially exhibited a highly adsorption efficient for DMP and 2, 4-DCP in the low concentrations region.

CONCLUSIONS

Highly microporous carbon adsorbent CR-1 was prepared from waste polysulfonated cation-exchange resin by CO\(_2\) activation. From SEM photographs, such CR-1 preserved the regular spherical shape of the polymer with a fraction of micropore area and volume of 0.825 and 0.868, respectively.

This study shows that CR-1 is an effective adsorbent for the removal of DMP and 2, 4-DCP from aqueous solution. Equilibrium adsorption data were fitted by four isotherm equations of Langmuir, Freundlich, PDM and Toth models. PDM and Toth models, which based on the theory of adsorption Polanyi, provided the best correlation for experimental data. The adsorption kinetics was found to follow the pseudo second order, controlled by intra-particle diffusion.

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