



Predicting the adsorption of organic pollutants from water onto activated carbons based on the pore size distribution and molecular connectivity index



Warisa Bunmahotama^a, Wei-Nung Hung^{b, c}, Tsair-Fuh Lin^{a, b, *}

^a Department of Environmental Engineering, National Cheng Kung University, Tainan 70101, Taiwan

^b Global Water Quality Research Center, National Cheng Kung University, Tainan 70955, Taiwan

^c Green Energy and Environment Research Laboratories, Industrial Technology Research Institute, Hsinchu 30011, Taiwan

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ABSTRACT

A new model approach is developed to predict the adsorption isotherms of low-molecular-weight nonpolar organic compounds (LMWNPOCs) onto activated carbons (ACs). The model is based on the Polanyi-Dubinin (PD) equation, with the limiting pore volume of adsorbent estimated from the pore size distribution (PSD) data, and the adsorption affinity of adsorbate described by the molecular connectivity index (MCI). To obtain the MCI parameters, the model was first tested for the adsorption of 34 LMWNPOCs primarily on F400 AC from 3 reports. The models fit the experimental data well, with only 39.2% of errors. The approach was further employed to predict the adsorption capacity of 40 LMWNPOCs on F400 AC, 12 LMWNPOCs onto 9 other ACs, and 8 LMWNPOCs onto 5 ACs with unknown PSD, with the errors of 41.9%, showing the model being reasonable. The model approach may provide a simple means for predicting adsorption capacities of LMWNPOCs onto different ACs.

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1. Introduction

Adsorption with activated carbon (AC) is a common technology to remove organic contaminants in water treatment. To design the adsorption process, the equilibrium contaminant adsorption isotherm has to be estimated in advance. The US Environmental Protection Administration (USEPA) estimates that there are 15,000 compounds manufactured in the U.S. in quantities greater than 10,000 pounds (USEPA, 2002). Many of these compounds may be present in different water-treatment systems. It is infeasible to directly measure the adsorption capacities (or isotherms) for all compounds of concern with many ACs of different properties, because such an experimental work would be too costly and time-consuming (Lee et al., 1981; Corapcioglu and Huang, 1987). Therefore, a model capable of predicting adsorption isotherms with reasonable accuracy based on specific properties of organic contaminants and ACs would relieve the experimental work to yield needed data for process design.

Many studies have been directed to construct models for estimating the adsorption capacities of organic contaminants onto ACs. However, no universal model has been successfully developed for all chemicals. The current developed models usually estimate the adsorption of compounds from a specific class based on the functional group (Crittenden et al., 1999), the hydrogen bonding capability (de Ridder et al., 2010), and/or the molecular size (Mezzari, 2006). In light that small-sized hydrocarbons and halogenated hydrocarbons are of a major concern in water treatment (USEPA, 2014) and in drinking water contamination (USEPA, 2015), a predictive model aimed for estimating the adsorption of these chemicals by ACs would be especially valued.

Prediction of adsorption capacities in pure water system involves both the properties of chemical and ACs. Polanyi–Dubinin (PD) equation is one of the models commonly employed to predict the adsorption isotherms of organic compounds from both vapor phase (Dubinin and Astakhov, 1971; Kapoor et al., 1989) and aqueous phase (Manes and Hofer, 1969; Manes, 1998; Rozwadowski et al., 1989; Stoeckli et al., 2001). The equation is a combination of adsorption potential theory developed by Polanyi (1920) and pore filling theory proposed by Dubinin and co-workers (Bering et al., 1966; Dubinin, 1985). The PD equation may be expressed as

* Corresponding author. Department of Environmental Engineering, National Cheng Kung University, Tainan 70101, Taiwan.

E-mail address: tflin@mail.ncku.edu.tw (T.-F. Lin).

$$W = W_0 \exp \left[- \left(\frac{\varepsilon}{\beta E_0} \right)^n \right] \quad (1)$$

where

- W = volume of solute adsorbed (mL/g),
- W_0 = the limiting volume of the adsorption space, i.e., the micropore volume (mL/g),
- E_0 = the characteristic adsorption energy of the reference adsorbate (cal/mol),
- β = affinity coefficient of the characteristic curve (–),
- n = the exponential constant (–),
- $\varepsilon = RT \ln (C_s/C)$ in aqueous system (cal/mol),
- C = the aqueous phase concentration (mg/L),
- C_s = the aqueous solubility (mg/L),
- R = the gas constant (1.987 cal/mol/K), and
- T = the absolute temperature (K).

The PD equation is widely used for adsorption on porous activated-carbon adsorbents, including the adsorption for gases with relative pressure >0.0015 (Ozawa et al., 1976; Hung and Lin, 2007), organic vapors with concentrations of 100–10,000 parts per million (in volume) (Noll et al., 1989), and organic contaminants in water with concentrations at the $\mu\text{g/L}$ – mg/L level (Crittenden et al., 1999). The PD equation requires only 3 parameters to determine the adsorption capacity. In the equation, $\beta \times E_0$ may be considered as one parameter, as it is only dependent on the properties of adsorbates. The other two parameters, W_0 and n , are only relevant to the nature of adsorbents used.

Attempt has been made by many researchers on the estimation of W_0 (Dubinin, 1989; Aukett et al., 1992). Based on the micropore volume-filling theory, Urano et al. (1982b) found that W_0 for vapor phase adsorption was approximately equal to 0.055 mL plus the micropore volume for pores with diameter less than 3.2 nm of different granular activated carbons (GACs). Hung and Lin (2007) also employed the same approach to obtain the W_0 for two ACs, which allowed the adsorption capacity to be reasonably predicted. Urano et al. (1982a) employed a similar approach for estimating W_0 of 16 organic compounds onto 5 GACs in aqueous solution. In their study, a modified Freundlich equation was developed to describe the adsorption isotherms, and both W_0 and the exponential parameter of the modified Freundlich equation were pore size dependent. Mezzari (2006) proposed that W_0 in aqueous phase, called the accessible pore volume in their study, may be estimated by the adsorption curves of reference compounds, such as nitrogen and carbon dioxide in gaseous phase, and benzene in aqueous phase. Hsieh and Teng (2000) measured the pore size distribution (PSD) of 4 GACs with different activation levels and linked the PSD information with W_0 of phenol in water. The above-mentioned results showed that the PSD data has the potential to be used to predict the adsorption capacity of organic compounds onto ACs.

The exponent, n , has also been studied extensively in both gaseous and aqueous phases. Dubinin and Astakhov (1971) showed that the exponent n varies between 1 and 3, depending on the nature of adsorbent used. The value of n approaches 3 for adsorbents with homogeneous micropores, whereas n approaches 1 for adsorbents with highly heterogeneous micropores. Crittenden et al. (1999) showed that range of n values for adsorption of organic chemicals from water on the activated carbons is from 1.05 to 1.61. Condon (2000a, b) suggested that n values in the PD equation depended on the methods used to treat the adsorption mechanisms. In case of heterogeneous adsorbent, the Dubinin and Astakhov (DA) model may be simplified to Dubinin-Radushkevich (DR) equation ($n = 2$) when the energy distribution of the surface follows lognormal

energy distribution with a standard deviation (σ) = 0.25, or to the Freundlich model ($n = 1$) if σ is equal to 0.5 (Condon, 2000a, b).

β is a measure of the similarities of the characteristic of adsorption between studied and reference adsorbates, and may be defined as E/E_0 (characteristic adsorption energy of the studied compound to the reference compound) (Dubinin, 1975). A few approaches have been proposed to link β with the properties of adsorbates, including parachor (Dubinin, 1960; Vaskovsky, 1950), polarizability (Dubinin and Sawerina, 1936) and molar volume (Vaskovsky, 1950; Dubinin and Tomofeyev, 1946).

In aqueous phase adsorption, the net attractive forces involve the solute, solvent, and the adsorbent. Crittenden et al. (1999) replaced $\beta \times E_0$ with a new term, called the normalizing factor (N), to account for the total interaction forces in aqueous system. In the study, N for different chemicals is described with linear solvation energy relationships (LSERs). LSERs (Kamlet et al., 1977) treat the solvation effect in solvent-solute systems, and usually four parameters, including intrinsic molar volume, the polarity/polarizability parameter, the hydrogen-bonding acceptor parameter, and the hydrogen-bonding donor parameter, were used (Crittenden et al., 1999; Luehrs et al., 1995). Luehrs et al. (1995) applied the LSERs to the prediction of partition constants for 353 organic compounds onto activated carbon from the aqueous phase. However, the errors between predictions and experimental data were relatively high, usually $>100\%$. Crittenden et al. (1999) applied LSERs with an improved prediction of the adsorption capacity of 89 organic compounds onto activated carbon by grouping the chemicals into three categories: halogenated aliphatic compounds, aromatics/halogenated aromatics, and poly-functional-group hydrocarbons. Mezzari (2006) employed quantitative structure–property relationships (QSPR) for the description of the affinity coefficient, β . Among the 14 models they developed, QSPR_4, which accounted for surface volume scaled, dielectric energy, highest occupied molecular orbital energy, and electrostatic hydrogen bond basicity, had the best-simulated results with the data. However, for the 62 compounds they simulated, four molecular size dependent sub-models are needed.

PD equation has been used since 1960 (Dubinin, 1960) for the adsorption in gaseous (Ozawa et al., 1976; Hung and Lin, 2007) and aqueous systems (Crittenden et al., 1999). Most studies link the adsorption data with chemical properties, such as molar volume (Manes and Hofer, 1969; Arbuckle, 1981; Manes and Wohleber, 1971; Wohleber and Manes, 1971; Kuennen et al., 1989), polarizability (Dubinin and Sawerina, 1936), parachor (Dubinin, 1960; Vaskovsky, 1950), and more recently LSERs (Crittenden et al., 1999). Only few studies investigated the influence of AC properties on the adsorption capacity (Urano et al., 1982b; Hsieh and Teng, 2000). Although attempts have been made to predict the adsorption capacity of organic compounds using purely the properties of ACs and chemicals (Li et al., 2005; Zhang et al., 2013), only very limited numbers of chemicals and ACs were examined and verified. In this study, a new approach was proposed to estimate the adsorption capacity of a compound onto AC using simply the properties of chemicals and the AC pore size distribution data. All predicted parameters were either obtained from literature or from chemical database and no advanced experiments are needed. The approach was validated with extensive adsorption data of 42 organic chemicals onto 15 different activated carbons from 12 published reports.

2. Methods

2.1. Modeling approach

The PD equation (Dubinin, 1960) modified by Crittenden et al.

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