THE EFFECTS OF ACTIVATED CARBON PHYSICAL AND CHEMICAL CHARACTERISTICS ON THE ADSORPTION ENERGY AND AFFINITY COEFFICIENT OF DUBININ-RAUSHKEVICH EQUATION

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Introduction

Microporous catalysts and adsorbents play crucial roles in chemical and environmental applications. Porosity analysis is an important aspect of the characterization of these materials. One of the most widely models used for micropore characterization is the Dubinin-Radushkevich (DR) equation, Eqn. (1), that was developed based on the theory of micropore filling:

$$V = V_0 \exp[-(\frac{RT \ln(P/P_0)}{E})^2] \qquad \text{Eqn. (1)}$$

Where V is the adsorbed gas volume at relative pressure of P/P_0; V_0 maximum volume of adsorbed gas in micropores; R the universal gas constant (0.0083144 kJ/K mol); T the analysis temperature (K); and E is the adsorption energy (kJ/mol). From the linearized plot of DR equation, V_0 and E are calculated. By using a conversion factor the equivalent liquid volume or micropore volume can be calculated from V_0. Often E is expressed as βE_0. β is a constant known as similarity or affinity coefficient, and E_0 is the adsorption energy of a reference vapor (usually benzene). β is an important parameter that is used in pore size distribution or average pore width calculations [e.g., 1-4]. Several correlations have been proposed to predict the value of β based on the physical properties of adsorbate and reference vapor [5]. This includes ratios of molecular polarizabilities or liquid molar volumes for adsorbate with respect to the reference vapor. All of the proposed correlations are independent of the adsorbent surface chemistry. This is based on the original assumption of Dubinin equation that: (1) adsorption forces are due to dispersion interactions (non-specific or non-polar interactions); and (2) the adsorbent surface behaves similarly for both adsorbate and reference vapors. Therefore, the effect of adsorbent surface on β (i.e., E/E_0) is canceled out.

In this paper the effect of adsorbent characteristics (i.e., porosity and surface chemistry) on the experimentally determined β and E_0 parameters of nitrogen (the most widely used gas for surface area and porosity characterization), trichloroethylene (TCE, an organic non-polar vapor), and water vapor (a polar vapor capable of interacting with the adsorbent surface through specific H-bond interactions) were investigated. Results of nitrogen studies can give more realistic values for β and E_0, therefore leading to a more

accurate porosity characterization. TCE and water vapor results can illustrate the effect of non-specific (TCE) or specific (water vapor) interactions between adsorbates and activated carbon surfaces on the parameters of DR equation.

Experimental

Adsorbents. Two granular (F400 and Macro) and three fibrous (ACF10, ACF15, and ACF20H) activated carbons were used in this study. F400 (Calgon Corp.) is a microporous, coal-based, and steam-activated, while Macro (Westvaco Inc.) is a mesoporous, wood-based, and phosphoric acid-activated carbon. Three phenol formaldehyde-based activated carbon fibers (American Kynol, Inc.) are microporous materials with relatively uniform pore size distributions.

F400, Macro, and ACF10 were modified to produce activated carbons with a wide range of physical and chemical characteristics. Modification protocols were performed by using a combination of: (i) heat-treatment under helium or hydrogen at 900°C for 2hr (**He or H**, respectively); (ii) oxidation with concentrated nitric acid (**16NO**), and (iii) ammonia treatment (at 400°C for 1hr; **4N1H**, 800°C for 1hr; **8N1H**, or 800°C for 2hr; **8N2H**). Details of these treatments can be found elsewhere [6]. The name of each modified activated carbon shows the original precursor that was modified according to the described treatment methods. For example, **ACF10,He,16NO,8N1H** is the ACF10 fiber that was heat-treated under helium followed by oxidation by concentrated nitric acid and finally treated by ammonia at 800°C for 1hr.

Adsorption isotherms. All adsorption isotherms were volumetrically obtained by using a Micromeritics ASAP 2010 instrument. Benzene, TCE, and water vapor isotherms were performed at 273.15K, while nitrogen isotherm data was collected at 77K.

Characterization of adsorbents. Various characterization methods have been used to determine physical and chemical characteristics of activated carbons. These methods are: (i) pH_{PZC} and total HCl and NaOH uptake for determination of carbons' surface acidity/basicity; (ii) X-ray Photoelectron Spectroscopy (XPS) for the surface elemental analysis; and (iii) Surface area and pore size distribution using the nitrogen isotherms. Details of these methods were described elsewhere [6].

Results and Discussion

Physicochemical characteristics. Physical and chemical characterization results of virgin and modified activated carbons are tabulated in Table 1. By using different types of granular and fibrous activated carbon precursors and applying various types of surface modifications, a number of activated carbons with different characteristics were produced. A concise discussion about properties of carbon adsorbents is presented below. A more detailed information about the characterization of the modified carbons can be found elsewhere [6,7].

Table 1. Physicochemical characteristics of activated carbons.

Carbon	SA_{BET}	$V_{micro, DR}$	V_{total}	W [a], Å		Pore volume distribution [b], %				pH_{PZC}	NaOH uptake	HCl uptake	O	N	C
	m^2/g	cm^3/g	cm^3/g	< 20Å	< 30Å	<7Å	7Å-10Å	10Å-20Å	>20Å		meq/g		atom%		
ACF10	963	0.382	0.374	6.8	6.8	76.43	14.65	8.92	0.00	8.6	0.156	0.294	4.1	0.8	94.6
ACF15	1459	0.587	0.585	8.1	8.1	48.16	23.88	27.76	0.20	8.7	0.117	0.425	4.4	0.6	94.6
ACF20H	1983	0.811	0.860	10.5	10.9	27.62	18.83	49.93	3.63	9.6	0.091	0.451	3.3	0.4	96.1
ACF10,He	1057	0.410	0.407	7.4	8.2	53.51	17.57	11.35	17.57	10.0	0.086	0.381	3.6	0.4	94.9
ACF10,H	1085	0.424	0.456	7.4	7.8	63.54	14.36	15.47	6.63	10.8	0.006	0.404	2.6	0.8	96.3
ACF10,He,16NO	768	0.302	0.305	8.1	8.1	48.92	22.51	28.57	0.00	1.9	3.046	0.000	13.3	2.5	83.4
ACF10,He,16NO,4N1H	1053	0.420	0.503	9.9	10.9	31.39	14.11	38.20	16.30	7.8	0.790	0.348	7.6	4.1	87.1
ACF10,He,16NO,8N1H	1272	0.509	0.606	10.2	11.1	32.60	12.60	39.20	15.60	9.7	0.291	0.488	3.8	2.7	91.7
F400	1035	0.404	0.553	9.6	10.7	27.29	18.57	27.07	27.07	8.5	0.238	0.411	5.9	0.5	92.3
F400,He,16NO	970	0.379	0.531	10.6	12.5	13.88	24.71	30.59	30.82	1.9	1.864	0.097	11.3	1.2	86.1
F400,He,16NO,8N2H	970	0.376	0.611	11.3	15.3	13.24	9.03	32.35	45.38	8.5	0.201	0.476	5.7	3.9	89.0
Macro	1569	0.567	1.282	11.7	16.5	9.20	1.24	22.83	66.73	1.9	1.232	0.000	7.5	0.7	90.6
Macro,He,16NO	1084	0.398	0.878	10.5	14.7	11.29	4.57	17.39	66.75	1.9	3.570	0.000	14.0	2.4	82.8
Macro,He,16NO,8N2H	1767	0.632	1.443	11.3	16.7	8.53	2.87	17.61	70.99	6.9	0.424	0.508	4.1	4.5	90.7

a. Average pore widths of activated carbons determined from DFT (Density Functional Theory) distribution results in <20Å and < 30Å ranges.
b. Determined from DFT.

ACF10, ACF15, and ACF20H are highly microporous fibers and their surface areas, micropore volumes, and average pore widths follow this order: ACF20H > ACF15 > ACF10. All of these virgin fibers show similar surface chemistries, as demonstrated by their pH_{pzc} and surface elemental analysis data. In comparison to virgin ACF10, heat-treated fibers (ACF10,He and ACF10,H) have slightly higher surface basicities, indicated by higher acid uptakes and pH_{pzc} values, and slightly larger surface areas and average micropore widths.

Nitric acid oxidation of heat-treated ACF10 significantly increased its surface polarity (demonstrated by a substantially higher oxygen content) and acidity. This treatment also increased the average micropore width and decreased surface area and micropore volume. Ammonia treatment of oxidized fiber at two temperatures produced fibers with larger average micropore widths (similar to ACF20H), higher surface area and pore volumes, and different levels of surface polarities (from the contribution of N- or O-containing functionalities).

F400 is a microporous GAC with low surface polarity. Its total surface area and surface acidity/basicity are similar to those of ACF10, but with a completely different pore volume distribution. The major difference of oxidized F400 (**F400,He,16NO**) with F400 is in its high surface polarity (high oxygen content). A slight increase in the average micropore width and a shift toward a less microporous structure are noticeable. **F400,He,16NO,8N2H** is a more mesoporous GAC with a wider average pore width, comparing to F400. Surface elemental analysis data of this carbon indicates existence of a considerable number of polar N- or O-containing functionalities on the surface. However, the overall surface polarity of this carbon appears to be lower than its immediate precursor (**F400,He,16NO**).

Macro is a mesoporous carbon having a polar and acidic surface. **Macro,He,16NO** shows a considerably lower surface area and pore volume and slightly smaller average micropore width than Macro. Based on the oxygen content values, surface polarity of oxidized Macro is significantly higher than its virgin precursor. Ammonia treatment of oxidized Macro produces a highly mesoporous carbon, but with an average micropore width value similar to that of Macro. Although the surface compositions of Macro and **Macro,He,16NO,8N2H** are different, based on their similar overall concentration of surface oxygen and nitrogen, they have similar surface polarities as indicated by their similar affinities for water (data not shown).

DR analysis of adsorption isotherms. Adsorption energies (E) of benzene, nitrogen, TCE, and water vapor were obtained from slopes of linearized DR plots (LogV vs. $Log^2(P/P_0)$) and reported in Table 2. By using the experimental values of adsorption energies, affinity coefficient of each vapor was also calculated and shown in Table 2. The linear behavior of DR equation was observed in different relative pressure ranges, depending on adsorbate and adsorbent characteristics. For benzene, nitrogen, and TCE the linear behavior was observed within: 10^{-2}-10^{-1}, 10^{-5}-10^{-1}, and 10^{-3}-10^{-1} ranges, respectively. As expected, for water, due to its incompatibility with the carbon surface, a

Table 2. Experimental values of E and β determined from linearized DR equations.

Carbon	E, kJ/mol				β			W [a], Å	
	C_6H_6	N_2	TCE	H_2O	N_2	TCE	H_2O	< 20Å	< 30Å
ACF10	27.223 (0.774)	9.443 (0.025)	30.843 (1.993)	3.736 (0.295)	0.347	1.133	0.137	6.8	6.8
ACF15	23.955 (0.793)	7.218 (0.049)	24.891	3.582	0.301	1.039	0.150	8.1	8.1
ACF20H	17.557 (0.866)	6.035 (0.051)	19.034	1.753	0.344	1.084	0.100	10.5	10.9
ACF10,He	27.041	8.659	27.502	2.917	0.320	1.017	0.108	7.4	8.2
ACF10,H	26.123	8.534	33.026	2.761	0.327	1.264	0.106	7.4	7.8
ACF10,He,16NO	23.646 (0.462)	7.715	25.008	4.763	0.326	1.058	0.201	8.1	8.1
ACF10,He,16NO,4N1H	24.224	6.646	20.165	4.076	0.274	0.832	0.168	9.9	10.9
ACF10,He,16NO,8N1H	21.922	6.532	20.331	4.020	0.298	0.927	0.183	10.2	11.1
F400	17.669	6.792	19.662	1.283 (0.001)	0.384	1.113	0.073	9.6	10.7
F400,He,16NO	14.543 (0.450)	6.425 (0.052)	15.496	2.717	0.442	1.066	0.187	10.6	12.5
F400,He,16NO,8N2H	11.009	5.676	11.972	1.266	0.516	1.087	0.115	11.3	15.3
Macro	10.066 (0.687)	5.378 (0.007)	11.377	1.365 (0.016)	0.534	1.130	0.136	11.7	16.5
Macro,He,16NO	11.443 (0.105)	6.036	11.905	2.829	0.527	1.040	0.247	10.5	14.7
Macro,He,16NO,8N2H	9.980	5.346	10.519	2.067	0.536	1.054	0.207	11.3	16.7

a. Average pore widths of activated carbons determined from DFT pore size distribution results in <20Å and < 30Å ranges.
Values in the parentheses represent calculated standard deviations of adsorption energies from different runs.

considerable amount of uptake was observed at higher relative pressures, in comparison to other tested adsorbates. DR plots of water vapor for some of activated carbons showed more than one linear region. The reported E values of fibrous and granular carbons were calculated within the relative pressure ranges of 0.6-0.9 and 0.4-0.7, respectively.

The linear correlation coefficients between E (or β) and average pore widths are calculated and tabulated in Table 3. Consistent with previous studies, for all nonpolar adsorbates (benzene, nitrogen, and TCE) regardless of adsorbents surface chemistry (surface composition or polarity), carbons with smaller average micropores showed higher adsorption energies (Table 2). For example, in the virgin activated carbon fiber series (ACF10, ACF15, and ACF20H), ACF10 with the smallest pore size showed the highest adsorption energy. This is also confirmed by relatively high correlation coefficients between adsorption energies of all carbons (with different characteristics) and their average pore width (Table 3).

A comparison of similar E values of two carbons with identical average micropore widths but different surface chemistries (e.g., **ACF10,He,16NO** having a very polar surface with ACF15 that has a nonpolar surface), can demonstrate the independency of adsorption energies of nonpolar adsorbates (benzene, nitrogen, and TCE) to the adsorbents surface chemistry.

For water vapor (a polar adsorbate capable of forming H-bonds with O or N of surface functionalities), when the surface chemistry of adsorbents is similar, with an increase in the average micropore width a decrease in the adsorption energy is observed. A side-by-side comparison of ACF10, ACF15, and ACF20H can be provided as an example (Table 2). Unlike the nonpolar adsorbates, the effect of surface chemistry (or polarity) on the water vapor uptake is very noticeable. Activated carbons with higher surface polarities show higher adsorption energies due to specific adsorbate-adsorbent interactions existed by formation of H-bonds. Overall, for water vapor a combination of two factors, namely average micropore width and surface polarity, determine the value of adsorption energy. E of water vapor can be maximized when the average micropore width is minimized and the surface polarity is maximized. In the series of activated carbons studied in this work, the oxidized and microporous **ACF10,He,16NO** that has an overall high surface polarity and small average micropore width, demonstrated to have the highest adsorption energy.

Table 3. Correlations between adsorption energy (E) and average pore width (W).

Adsorbate	Linear correlation coefficient (R^2)			
	E vs. $W_{<20Å}$	E vs. $W_{<30Å}$	β vs. $W_{<20Å}$	β vs. $W_{<30Å}$
Benzene	0.8265	0.9093	-------	-------
Nitrogen	0.9738	0.9289	0.5090	0.7670
TCE	0.8853	0.9036	0.0506	0.0074
Water vapor	0.3620	0.3727	0.0512	0.0923

Note: Average pore widths of activated carbons determined from DFT pore size distribution results in <20Å and < 30Å ranges.

β values of nitrogen for different carbons were observed to vary in the 0.274-0.536 range. Results indicated that more mesoporous carbons had higher β_{N2} values (Table 2). However, no strong linear correlation between β_{N2} and average pore widths was observed. Consistent with the independency of adsorption energies of nitrogen and benzene from surface polarity, no correlation between β_{N2} and surface composition of carbons was observed.

It should be emphasized that using a constant β_{N2} value (e.g., 0.318, as used in the available classic surface area and pore size distribution softwares) for a mesoporous activated carbon, such as Macro, can lead to a considerable error in pore size distribution calculations using Medek or DRS equations [1,2]. Some researchers prefer to use the Stoeckli correlations [3,4] (e.g., $L = 10.8/(E_0 - 11.4)$ where L is the average pore width in nm, and E_0 is the characteristic energy, in kJ/mol) to directly estimate the average pore width from the characteristic energy (adsorption energy of benzene). Often the characteristic energy is calculated by using a constant β_{N2} value (e.g., 0.318) and adsorption energy of nitrogen as: $E_0 = E/\beta_{N2}$. This is evident that an error in the assumed value of affinity coefficient leads to an inaccurate estimation of E_0 and eventually average micropore width.

Obtained β_{TCE} values varied in the 0.832-1.264 range, apparently independent of surface chemistry or porosity of activated carbons. For 11 out of total 14 studied activated carbons β_{TCE} varied in a relatively small rage of 1.017-1.133 (Table 2). Independency of β_{TCE} from the surface chemistry of carbons is consistent with the previously discussed behavior of adsorption energies of TCE and benzene. Adsorption energies of both TCE and benzene correlate with the average micropore width, but their ratios (β_{TCE}) do not. This may be interpreted by the similarity in the adsorption mechanism of benzene and TCE molecules. Both TCE and benzene have planar structures with similar approximate sizes of 6.6Å×6.2Å×3.6Å [7] and 6.5Å×6.5Å×3.7Å (two dimensions of benzene are calculated from the reported flat molecular area of 43Å^2) [8], respectively.

β_{H2O} values of granular carbons changed in the range of 0.073-0.209 depending on the surface chemistry and apparently independent of the carbon porosity. In most cases, carbons with more oxidized or more polar surfaces showed higher β_{H2O} values.

Conclusions

Several surface-modified granular (both coal- and wood-based) and fibrous activated carbons with different physicochemical characteristics were utilized to study the adsorption of nitrogen, benzene, trichloroethylene (TCE), and water vapor. The dependency of adsorption energy (E) and affinity coefficient (β) of Dubinin equation on the surface chemistry and porosity of these activated carbons was investigated.

Consistent with previous studies, for all nonpolar adsorbates (benzene, nitrogen, and TCE) regardless of adsorbents surface chemistry (surface composition or polarity),

carbons with smaller average micropores showed higher adsorption energies. For water vapor (a polar adsorbate capable of forming H-bonds with O or N of surface functionalities), when the surface chemistry of adsorbents was similar, with an increase in the average micropore width a decrease in the adsorption energy was observed. Unlike the nonpolar adsorbates, the effect of surface chemistry (or polarity) on the water vapor uptake was very noticeable. Activated carbons with higher surface polarities showed higher adsorption energies due to specific adsorbate-adsorbent interactions existed by formation of H-bonds.

β_{N2} for different carbons were observed to vary in the 0.274-0.537 range. Results indicated that more mesoporous carbons had higher β_{N2} values, while no dependency was observed between this parameter and surface chemistry of carbons. In most cases, β_{TCE} values varied in the 1.017-1.133 range, apparently independent of surface chemistry or porosity of activated carbons. β_{H2O} values of granular carbons changed in the range of 0.073-0.209 depending on the surface chemistry and apparently independent of the carbon porosity. In most cases, carbons with more oxidized or more polar surfaces showed higher β_{H2O} values.

The independency of adsorption energies of benzene, nitrogen, and TCE, as well as β_{N2} and β_{TCE} from surface chemistry of the carbons confirmed the significance of only nonspecific interactions between these non-polar adsorbates and carbon surface. While in the case of polar water molecules, the dependency of E_{H2O} and β_{H2O} to the surface chemistry of adsorbents clearly indicated the importance of specific forces (e.g., hydrogen bonding or electrostatic interactions).

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