Journal of Colloid and Interface Science 332 (2009) 515–519

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Short Communication

Assessment of the surface area occupied by molecules on activated carbon from liquid phase adsorption data from a combination of the BET and the Freundlich theories

Nady Passé-Coutrin, Sandro Altenor, Sarra Gaspard *

Laboratoire COVACHIMM, EA 3592 Université des Antilles et de la Guyane, BP 250, 97157 Pointe à Pitre Cedex, Guadeloupe, France

ARTICLE INFO

Article history:
Received 8 August 2008
Accepted 27 December 2008
Available online 10 January 2009

Keywords:
Liquid phase adsorption
Freundlich isotherm
Surface area
BET isotherm

ABSTRACT

A new equation is derived from a combination of the BET (Brunauer, Emmett, Teller) and Freundlich isotherms fitted for liquid phase adsorption data on activated carbons. This equation, depending on the Freundlich parameters and the equilibrium adsorption–desorption constant can be used for assessment of the surface area occupied by the solute molecules on a surface in a liquid phase system under some conditions.

1. Introduction

In a recent work [1] the empirical linear relationship between the BET surface area S_{BET} and the Freundlich constant K_F, calculated from nitrogen adsorption isotherms of activated carbons (ACs), $S_{BET} = a_0 K_F$ was mathematically demonstrated. There is a relative pressure domain, in which both equations, can give an estimation of the same value of number of molecule adsorbed on the surface. It was demonstrated that such a correlation exists in the relative pressure domain in which the BET equation [2] is valid, whatever the value of c for the BET equation and for values of the Freundlich exponent, α, between 0 and 0.2 and for P/P_0 values lower than 0.3. This later study allowed us to propose a new method for calculation of the specific surface area depending on α and K_F, where K_F is the Freundlich constant and α the Freundlich exponent of the Freundlich isotherm [3]. In the present work an attempt for calculating the specific surface area occupied by two solutes methylene blue (MB) and phenol respectively on ACs surfaces is done from their liquid phase adsorption data.

2. Materials and methods

2.1. Preparation of activated carbons

The ACs were obtained from vetiver roots and sugar cane bagasse respectively, collected in Guadeloupe, French West Indies. These materials were initially dried at 105 °C for 48 h using a drying oven, then ground and sieved to several particle sizes ranging from less than 0.2 to 1 mm. The fraction with a particle size ranging between 0.4 and 1 mm was used for carbonization. In this experiment, two conventional methods of preparation of ACs were used.

For physical activation, approximately 5 g of pre-treated vetiver roots or sugar cane bagasse were initially pyrolyzed in a furnace Thermolyne F-21100 under nitrogen atmosphere at 800 °C for 1 h with a heating rate of 10 °C/min. Carbon thus prepared, were then activated with steam under a nitrogen atmosphere at 800 °C for 8 h with a heating rate of 10 °C/min in the same furnace giving sample vet-H_2O and BagH_2O.

For chemical activation, 3 g of the raw material was impregnated in phosphoric acid (H_3PO_4) 85% for 24 h. Impregnation ratios X_P (g H_3PO_4/g precursor): 0.5:1, 1:1 and 1.5:1 were used giving samples: VetP0.5, VetP1, VetP1.5, BagP1 and BagP1.5 respectively. After impregnation, the samples were dried for 4 h at 110 °C in a drying oven. The samples thus dried were pyrolyzed under a nitrogen flow at 600 °C for 1 h. After cooling, until ambient temperature, the ACs thus obtained were washed with distilled water until stabilization of the pH, and then dried overnight using a drying oven at 110 °C.

2.2. Textural characterization of ACs

The BET surface area and porous properties of each AC were determined from N_2 adsorption experiments. The ACs were characterized by N_2 adsorption at 77 K using a Micromeritics model ASAP-2020 analyzer. The carbon sample was degassed for 24 h

---

* Corresponding author. Fax: +590 590 48 30 72.
E-mail address: sgaspard@univ-ag.fr (S. Gaspard).

0021-9797/$ – see front matter © 2009 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcis.2008.12.079

Table 1
Physical properties deduced from N_2 adsorption at 77 K on ACs prepared from vetiver roots and sugarcane bagasse by steam activation and chemical activation with phosphoric acid.

Samples	S_{BET} (m^2/g)	S_{mi} (m^2/g)	S_{mi}/S_{BET} (%)	S_{ext} (m^2/g)	V_{mi} (cm^3/g)	V_{me} (cm^3/g)	V_{tot} (cm^3/g)	V_{mi}/V_{tot} (%)
$VetH_2O$	1185	894	75	291	0.36	0.33	0.69	52
VetP0.5	1170	1017	87	153	0.45	0.31	0.76	59
VetP1	1272	737	58	535	0.39	0.80	1.19	33
VetP1.5	1004	468	46	536	0.22	0.80	1.02	21
BagP1	1502	911	60	591	0.45	0.81	1.26	35
BagP1.5	1492	327	22	1165	0.14	1.49	1.63	8

at 573 K to remove any moisture or adsorbed contaminants that may have been present on their surface. The manufacturer's software provided BET surface area (S_{BET}) of the carbons by applying the BET equation to the adsorption data. The microporous surface (S_{micro}) and external surface (S_{ext}), the total pore volume (V_T) and micropore volume (V_{mi}) were evaluated by t-plot method, and mesopore volume (V_{me}) was estimated by Barrett–Joyner–Halenda (BJH) method [4]. The textural characteristics of the samples are given in Table 1 and carefully described in our recently published paper [1].

For adsorption equilibrium experiments, a fixed carbon concentration (40 mg) was weighed into 200 ml conical flasks containing 100 ml of different initial concentrations (50–300 mg/l and 20–100 mg/l) of methylene blue and phenol respectively, agitated at 200 rpm and at 25 °C using a magnetic agitator until equilibrium was obtained. The equilibrium time was preliminary determined by kinetic tests. After filtration, the concentration of each solute was determined with a UV/visible spectrophotometer (Anthelie Advanced 5 Secoman) at 271 nm and 658 nm for phenol and methylene blue respectively. Each experiment was repeated two times under identical conditions. The amount of adsorption at equilibrium, $q_e = V(C_0 - C_e)/W$ (mg/g), was calculated, where C_e is the equilibrium solute concentration (mg/g), C_0 is the concentration at the start time, respectively, V the volume of aqueous solution and W the mass of AC.

3. Results and discussion

The liquid phase BET isotherm [2,5,6] is the following:

$$q = q_m \frac{b_s C_e}{(1 - b_L C_e)[1 - b_L C_e + b_s C_e]}. \tag{1}$$

q_m (mg/g) is the amount of adsorbed phenol or dye per unit weight of AC, C_e is the solute equilibrium concentration, b_s is the equilibrium constant of adsorption on the first layer, b_L the equilibrium adsorption–desorption constant for upper layers of adsorbate on the adsorbent [6].

Consider the liquid phase Freundlich isotherm [3]:

$$q = K_F \times C_e^{1/n}. \tag{2}$$

K_F is the Freundlich constant and $1/n$ the Freundlich exponent obtained from the liquid phase adsorption isotherm.

Figs. 1A and 1B show the adsorption isotherm of methylene blue and phenol respectively onto the activated carbons. The adsorption data where fitted using the BET and Freundlich isotherm and the parameters obtained were reported in Tables 2 and 3. Fig. 2 shows the comparison between the experimental data and the Freundlich and BET fit for adsorption of MB on the VetP1.5 sample. As can be seen at lower concentration a better agreement is found with the BET, then for concentrations higher than 50 mg/L the experimental data are closer to the Freundlich fit.

Similarly to what observed in gaseous system [1] and according to Fig. 2, in a given concentration range, an equivalent amount of adsorbed molecules can be calculated using both expressions, the following equality can thus be written:

$$K_F \times \left(\frac{1}{b_L}\right)^{1/n} (b_L C_e)^{1/n} = q_m \frac{\frac{b_s}{b_L} b_L C_e}{(1 - b_L C_e)\left[1 + \left(\frac{b_s}{b_L} - 1\right) b_L C_e\right]}. \tag{3}$$

In Eq. (1) $b_L C_e$ replace the P/P_0 parameter used for gaseous system. Consequently K_F of Eq. (1) can be replaced by $K_F \times (1/b_L)^{1/n}$ and $1/n$ replace α. A Freundlich surface area S_F for liquid phase system can be deduced:

$$S_F = \frac{1}{M_A} S_A N \frac{(n)}{(n+1)^{(1+1/n)}} K_F \left(\frac{1}{b_l}\right)^{1/n}. \tag{4}$$

N is the Avogadro number, S_A the area of one solute molecule A on the sorbent surface, and M_A the molecular mass of the molecule A.

b_L, but also q_m and b_s, can be obtained by fitting the following quadratic equation:

$$\frac{C_e}{q} = \frac{1}{q_m b_s} + \frac{1}{q_m b_s}(b_s - 2b_L)C_e - \frac{b_L}{q_m b_s}(b_s - b_L)C_e^2. \tag{5}$$

Hence

$$\frac{C_e}{q} = aC_e^2 + bC_e + c \tag{6}$$

with

$$a = -\frac{b_L}{q_m}\left(1 - \frac{b_L}{b_s}\right), \tag{7}$$

$$b = \left[1 - \frac{2b_L}{b_s}\right]\frac{1}{q_m}, \tag{8}$$

$$c = \frac{1}{q_m b_s}. \tag{9}$$

The fit of our adsorption data with Eq. (5) allows us to determine a, b and c.

Equations (7), (8) and (9) give b_L from the following quadratic equation:

$$cb_L^2 + bb_L + a = 0.$$

Its solution is the positive roots

$$b_L = \frac{-b + \sqrt{b^2 - 4ac}}{2c} \tag{10}$$

giving

$$b_s = b_L - \frac{a}{cb_L} \tag{11}$$

and

$$q_m = \frac{1}{cb_s}. \tag{12}$$

When $b_L \ll b_s$,

$$b_L = -\frac{a}{b}, \qquad b_s = \frac{b}{c} - \frac{2a}{b}.$$