Environmental insights from Langmuir adsorption site capacities

Elham A. Ghabbour*, Geoffrey Davies

Department of Chemistry and Chemical Biology, Northeastern University, Boston, MA 02115, USA

ARTICLE INFO

ABSTRACT

Adsorption by soil humic acids (HAs) regulates the bioavailability of nutrients and pollutants, and adsorption studies can lead to useful environmental models. Langmuir's model of reversible adsorption of a gas on a solid surface as it applies to adsorption of a dissolved substance B on insoluble adsorbent A to give insoluble state $A \cdot B$ is examined in terms of the measured site capacity v_{obsd} (mmol solute/g adsorbent) at equilibrium concentration $[B]$, adsorbent site capacity v at infinite concentration $[B]$, and the maximum site capacity of the adsorbent, v_{max}. The relationship $v = S m_f v_{max} = S/\langle M_w \rangle$, where S is the number of solute entities per adsorbent site, m_f is the mass fraction of adsorption sites and $\langle M_w \rangle$ is the adsorbent's mass-average molar mass, is discussed. This relationship is applied to analysis of (1) different adsorption sites on a solid, municipal compost-derived HA and on a proposed HA building block, (2) adsorption of herbicide acifluorfen on a solid HA and (3) adsorption of herbicides alachlor and metachlor on activated charcoals. Practical applications of the relationship are listed.

1. Introduction

Soil serves many functions, among which is adsorption of solutes and metals carried by water through the land. Adsorption influences the bioavailability of nutrients as well as pollutants [1]. Long-lived [2], solid organic soil components called humic acids (HAs), the products of plant and animal decay in a process called humification [3], play a major role in soil adsorption processes, some of which are well described by a model first applied to heterogeneous catalysis by Langmuir [4]. This model has both thermodynamic character through an adsorption equilibrium constant and stoichiometric character from the site capacity (the number of adsorption sites per gram of HA and the fraction of them that are occupied). As such, the Langmuir model is an excellent tool for distinguishing between thermodynamic and stoichiometric factors in soils and sediments, which are crucial natural systems that sustain life on Earth. Here we focus on site capacities for adsorption by humic acids and activated charcoals.

2. The Langmuir adsorption model

Langmuir's original mode1 [4], which describes reversible adsorption of a gas on a solid surface, can also be applied to adsorption from solution of a substance B on a site of an insoluble adsorbent A at fixed temperature, Eq. (1). Here, $A \cdot B$ (s) is the insoluble solute state and K is the equilibrium constant for adsorption.

$$A(s) + B(aq) \rightleftharpoons A \cdot B(s) \quad K \tag{1}$$

The fraction θ of adsorbent sites occupied by B is given by Eq. (2), where $[B]$ is the concentration of un-adsorbed B in solution at equilibrium.

$$\theta = \frac{K[B]}{1 + K[B]} \tag{2}$$

Eq. (3) is an alternative form of Eq. (2) [4–6]. Here, v_{obsd} is the observed site occupancy at a particular equilibrium concentration $[B]$ and v is the value of v_{obsd} when all the adsorbent sites are occupied at fixed temperature. We see that $\theta \rightarrow 1$ in Eq. (2) and $v_{obsd} \rightarrow v$ in Eq. (3) as $[B]$ increases.

$$v_{obsd} = \frac{K v [B]}{1 + K[B]} \tag{3}$$

Site capacity v_{obsd} under fixed conditions is measured as follows. A known mass of adsorbent is contacted with a known volume of a solution of known concentration $[B]_T$. After equilibrium is reached, $[B]$ is measured and subtracted from $[B]_T$. The result is multiplied by the solution volume to give the number of moles of B adsorbed. Dividing the result by the adsorbent mass gives v_{obsd}, which has units of moles/g adsorbent (or, in most systems, mmol solute/g adsorbent). The plot of v_{obsd} *vs.* $[B]$ at fixed temperature is an isotherm [4,7,8].

Inversion of Eq. (3) gives Eq. (4). If the Langmuir model fits the isotherm data, a plot of $1/v_{obsd}$ *vs.* $1/[B]$ should be linear with slope $1/Kv$ and intercept $1/v$. Then v and K are calculated and the isotherm

* Corresponding author. Tel.: +1 617 373 7988; fax: +1 617 373 8795.
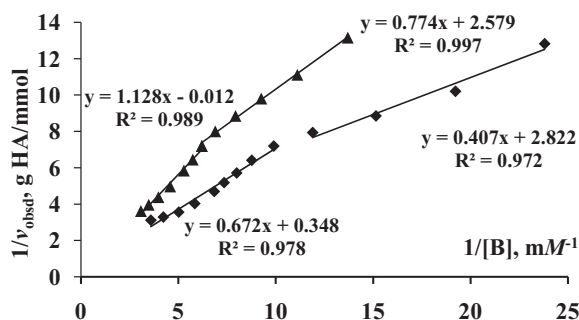 *E-mail address:* e.ghabbour@neu.edu (E.A. Ghabbour).

Fig. 1. Plot of Eq. (4) in steps II and III of adsorption of cytosine (diamonds) and cytidine (triangles) on municipal compost-derived HA at 10.0 °C [9].

Fig. 2. Plots of Eq. (7) with (a) $S = 1$ and (b) $S = 2$ in reactions (5), (6), (8) and (9), respectively. The "practical" v_{max} with BeO as the alkaline earth metal adsorbent with the smallest molar mass in reaction (6) is shown with dash-dotted lines.

is a Langmuir or L-curve. A non-linear plot of Eq. (4) eliminates Eq. (3) as an

$$\frac{l}{v_{obsd}} = \frac{l}{Kv[B]} + \frac{l}{v} \tag{4}$$

appropriate data-fitting function. The observed isotherm is then classified as a C-, H- or S-curve based on its appearance. Analysis of C-, H- or S-curves is semi-quantitative and can lead to different interpretations [5–8].

A value $\theta = 0.99$ in Eq. (2) means that 99% of the adsorbent sites are occupied, which occurs when $[B] = 99/K$. So, if $K = 21$ (the average value of K_i for adsorption of nucleic acid constituents such as adenosine on site i of a solid municipal compost-derived HA at 25.0 °C [9]), then $[B] = 4.7 M$. Compost-derived HA has at least three different adsorption sites $i =$ I, II and III [9,10]. Use of $[B] = 4.7 M$ in that system would saturate all three sites I–III and might even break the HA particles into soluble fragments [9,10].

The beauty of Langmuir Eq. (4) is that the intercept is l/v_I or l/v_{II} or l/v_{III}, depending on which HA adsorption step is being analyzed (Fig. 1) [9,11]. These are the apparent solute-binding capacities of the respective adsorbent sites under study. Their magnitudes (mmol solute/g HA) theoretically are independent of the solute molar mass, as found for solute families such as thymine, thymidine and thymidine-5′-monophosphate [11]. Another property of v is that $v = S/\langle M_w \rangle$, where $\langle M_w \rangle$ is the mass-average molar mass of the adsorbent and S is the number of solute entities adsorbed per site, as discussed below.

3. The stoichiometric character of site capacities

The stoichiometric character of site capacities can be illustrated with simple examples. Eq. (5) is the stoichiometric reaction of CO_2 with a hypothetical isolated oxide site and Eq. (6) (M = Be, Mg, Ca, Ba) describes stoichiometric CO_2 reactions with oxide sites in alkaline earth metal oxide adsorbents. Here, M are regarded as non-adsorptive diluents of the oxide sites. For practical purposes, v_{max} can be defined as the maximum site capacity of the adsorbent with the lowest molar mass ($\langle M_w \rangle_{BeO} = 25.0$ g/mol in Eq. (6)). Practical v_{max} for reaction (6) is indicated with dash-dotted lines in Fig. 2a. This distinction is unnecessary for undiluted elemental adsorbents such as carbon (see below).

$$O^{2-}(s) + CO_2(g) \rightarrow CO_3^{2-}(s) \tag{5}$$

$$MO(s) + CO_2(g) \rightarrow MCO_3(s) \tag{6}$$
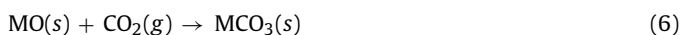
The site capacity v in reaction (5) is 1 mol CO_2/16.0 g O^{2-} or 62.5 mmol/g. The site capacity v of reaction (6) (M = Be) is 1 mol CO_2/25.0 g = 40.0 mmol/g BeO and the values with M = Mg, Ca and Ba are 24.8, 17.8 and 6.5 mmol/g metal oxide, respectively. The mass fractions m_f of O^{2-} sites in the oxide adsorbents with no metal present and with M = Be, Mg, Ca and Ba are 1.0, 0.64, 0.40, 0.28$_5$
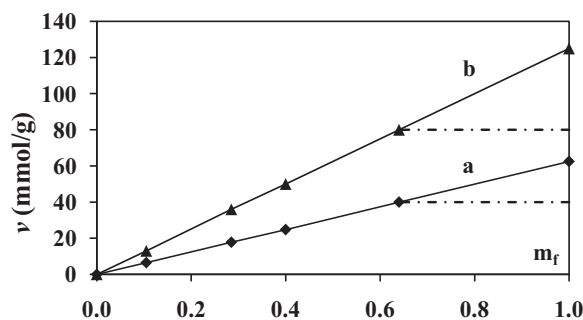
and 0.10$_5$, respectively. The site capacities are plotted as v vs. m_f in Fig. 2a. The value of v with $m_f = 1.0$ is the maximum theoretical site capacity v_{max}, which also is the slope of Fig. 2a. From this we obtain Eq. (7). Here, S is the number of solute molecules per adsorption site, v, m_f, and v_{max} are defined above and $\langle M_w \rangle$ is the mass-average molar mass of the adsorbent. $S = 1$ for reactions (5) and (6). This definition of $\langle M_w \rangle$ encompasses systems with polydisperse adsorbents such as humic acids [2,3].

$$v = S m_f v_{max} = S/\langle M_w \rangle \tag{7}$$

Reactions (8) and (9) consume two H atoms per oxide site (charge omitted) and the corresponding v_{max} with the metal oxides of reaction (6) are 80, 50, 36 and 13 mmol/g adsorbent at the same respective oxide site mass fractions m_f as before. The plot in Fig. 2b shows that $S = 2$ and that Eq. (7) is the general equation that relates v to v_{max} and $\langle M_w \rangle$ for an adsorption process.

$$O(s) + 2H(g) \rightarrow H_2O(l) \tag{8}$$

$$MO(s) + 2H(g) \rightarrow M(s) + H_2O(l) \tag{9}$$
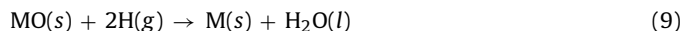
Suppose we measure a CO_2 adsorption isotherm with solid adsorbent BeO(s) in reaction (6), plot Eq. (4) and obtain $v = 4.4$ mmol CO_2/g BeO. Substitution of $v = 4.4$ and $v_{max} = 40$ mmol CO_2/g BeO with S = 1 into Eq. (7) gives $m_f = 0.11$. This means that only 11% (w/w) of the oxide sites in the BeO adsorbent are accessible to CO_2 at the experimental pressure and temperature.

4. v_{max} for a humic acid building block

Humic acids are made from the molecules present or accumulated at the HA source. This leads to the expectation that HAs are heterogeneous, with different structures made from different building blocks depending on the source [12–14]. However, the C, H, N and O element contents of well-purified HAs [15–19] and the types (alcohol, amine, carbonyl, carboxylic acid, phenol, quinone) and amounts of their functional groups (Table 1) [19–23] do not seem to vary greatly from sample to sample [24]. This suggests that HAs have a small or homologous range of similar building blocks. Fig. 3 shows two of the suggested ones and Table 2 lists their analytical properties. Structure **2** (Fig. 3) is a modified form of proposed HA building block **1** [24]. It fits the average element and functional group data of marine and terrestrial HA in Table 1. We will now derive v_{max} for proposed HA building block **2**.

Structure **2** has 13 functional groups and a molar mass of 765 g/mol. If one mole of a substance (e.g. adenine) reacts with each of the thirteen functional groups, then 13 moles of the substance are adsorbed and the structure is saturated. Therefore, v_{max} for this structure is given by Eq. (10).

$$v_{max} = 13,000 \text{ mmol}/765 \text{ g HA} = 17.0 \text{ mmol/g HA} \tag{10}$$