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Equilibrium isotherm simulation of tetrachlorethylene on activated carbon using the double layer model with two energies: Steric and energetic interpretations

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ABSTRACT

In this paper, the adsorption isotherms of tetrachlorethylene (PCE) on activated carbon at different temperature were simulated and interpreted using the double layer model with two energies. The formulation of this model was based on statistical physics formalism. Steric and energetic parameters related to the adsorption process were introduced in this model, such as the number of molecules per site (n), the receptor sites density N_M and the concentrations at half saturation c_1 and c_2. These parameters were deduced by numerical simulation of the adsorption isotherms and interpreted at different temperatures. Thermodynamic functions of adsorption process, i.e., entropy, free enthalpy and internal energy were computed and their negative values indicate that the adsorption is exothermic and spontaneous.

1. Introduction

The increasing environmental pollution from domestic and industrial effluents, particularly in the developing countries, is a problem of major concern. According to the USEPA, Tetrachloroethylene (PCE) is an organo-chlorinated compound produced and released into the environment at greatest extent [1,2]. For its high solvent power, PCE is widely used in several industries (mainly in textile dying and dry cleaning, metal degreasing and as extracting agent), also due to its non-flammability. However, when discharged into the environment, PCE can be considered as one of the most dangerous pollutants, due to its high toxicity and persistence grade [3]. Hence, the development of cost-effective and environmentally acceptable techniques for its elimination is a pressing need. Waters contaminated by organic chemicals can be treated manly by adsorption on activated carbons, thanks to a good pollutant removal capacity and a great versatility [4,5]. The knowledge of adsorption isotherms as well as of reliable adsorption models plays an important role in the analysis and design of adsorption systems. The performance of an adsorption treatment mainly depends on the thermodynamic aspects of solute-solvent-sorbent interactions and on the transport phenomena involving the diffusive-convective transport within the porous media. In an earlier work, Erto et al. [6] proposed the modeling of adsorption isotherms of PCE on activated carbon using empirical or semi-empirical models, such as the Langmuir and Freundlich models. In this paper, we focused our attention on the use of statistical physics to obtain new interpretation of the adsorption phenomena.

To this aim, experimental PCE adsorption isotherms were interpreted by the double layer model with two energies, established by the statistical physics. One of the advantages of applying this theory is to give a physicochemical meaning to the parameters involved in the model and then to provide new interpretations of the adsorption process at molecular level. The model was applied for the first time to the adsorption of organic compounds in liquid phase and allowed new physical interpretations at microscopic levels. The statistical model was also used to calculate thermodynamic functions which govern the adsorption phenomenon such as entropy, free enthalpy and internal energy.

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2. Materials and methods

2.1. Activated carbon characteristics

Aquacarb 207EA™ is a commercially available non impregnated granular activated carbon, product by Sutcliffe Carbon starting from a bituminous coal. The BET surface area is 950 m^2/g and the average pore diameter is 24 Å. Its chemical composition reveals high ash content (9.58%) and the value of the $pH_{PZC} = 8.0$ shows that the activated carbon has a slightly basic nature. A complete list of chemical and physical characteristics is reported in Di Natale et al. [7].

2.2. Adsorption isotherms

The samples for the adsorption tests were prepared by adding the analyte PCE (99.0%, Sigma Aldrich) to a commercial mineral water having a composition typical of groundwater (pH = 8 and a salinity of 0.46 mM). Isotherm experiments were conducted in a controlled thermostatic oven, using glass vessels as batch reactors. The sample solutions were prepared by adding the analyte and activated carbon to 200 ml amber stained, headspace-free glass vessels of mineral water. Then, they were sealed with a Teflon cap and covered with an aluminum sheet to prevent photo-degradation phenomena. Preliminary tests showed that a contact time of 72 h is required to reach equilibrium conditions. After equilibration, both the PCE concentrations in solution (c) and the PCE adsorbed on the carbon surface (Q) were measured; to such a purpose, the carbon is leached with 200 ml of acetone for a complete PCE extraction, following the EPA methods for soil analysis (EPA 5035). Then the PCE concentration in the leachate was determined. The experimental run accuracy is checked by allowing a maximum error of 5% in the PCE mass balance. The analyte solution concentrations were measured using a gas chromatograph (Agilent, GC 6980) equipped with a capillary column (DB-624, 30 m × 0.32 mm × 1.8 μm), an electron capture detector (ECD) and a Purge and Trap system (Tekmar LSC-2000) GC-connected. Analytical methods comply with the EPA method 5030B.

3. Theory: double layer model with two energies

The following statistical treatment here presented is applicable to both liquid and gas systems. As a first approximation, the mutual interaction between the adsorbed molecules is neglected [8–10] and their concentrations will be considered as relatively low. In order to employ statistical physics methods to derive the adsorption model, we consider that a variable number of molecules are adsorbed onto N_M receptor sites located on a unit mass of the adsorbent. In general, the adsorption reaction of liquid molecules *(A)* onto receptor sites *(S)* should include a stoichiometric coefficient *(n)*, as the following equation [8–10]:

$$nA + S \rightleftarrows A_nS \tag{1}$$

The parameter n is an average number, which can be an integer or not, greater or lower than 1. If n is greater than 1, it represents the number of molecules anchored on one site, corresponding to a multimolecular adsorption [10]. In this case, the coefficient could refer to an aggregation parameter representing the number of molecules which would be linked in the solution just before the adsorption and which would be adsorbed on the receptor site as an aggregate [10].

If n is lower than 1, it represents "the fraction of molecule per site" [10], and it corresponds to a multianchorage adsorption. In this case, we define the anchorage number $n' = 1/n$ which represents the number of sites occupied by one molecule. For example, if $n = 0.5$, then $n' = 2$ (one molecule anchored onto two sites).

The number n can also give information about the incidence to the adsorbent surface. Indeed, for $n < 1$, the molecule is anchored with more than one link, hence it is oriented parallel to the surface. If $n > 1$, more than one molecule is adsorbed on the same site, so that the molecule is oriented with an angle to the adsorbent surface. In Fig. 1, we give a simple example of the PCE anchorage on activated carbon.

Moreover, it assumed that adsorption isotherm can reach a saturation condition. Under these hypotheses, the isotherms can be simulated with a monolayer model or with a model that simulate the formation of two or more layers. As explained in details in following section, the use of the double layer model with two energies resulted as the most adequate to approximate the PCE adsorption experimental data. The assumptions used and the theoretical treatment using statistical model are here presented and discussed.

The starting point is the grand canonical partition function describing the microscopic states of a system, following the physical condition in which this system is placed. For the double layer model with two energies, we suppose that the first adsorbed layer has an adsorption energy level ε_1 while the second layer has a different adsorption energy level ε_2, which is supposed to be lower than the first, since the first molecules are adsorbed directly onto the surface. The partition function can be written according the following expression [10]:

$$z_{gc} = 1 + e^{\beta(\varepsilon_1+\mu)} + e^{\beta(\varepsilon_1+\varepsilon_2+2\mu)} \tag{2}$$

Where μ is the chemical potential of the receptor site and β is defined as, $1/k_BT$ where k_B is the Boltzmann constant and T is the absolute temperature. The total grand canonical partition related to N_M receptor sites per surface unit, which we assume identical and independent, is then written as:

$$Z_{gc} = (z_{gc})^{N_M} = \left(1 + e^{\beta(\varepsilon_1+\mu)} + e^{\beta(\varepsilon_1+\varepsilon_2+2\mu)}\right)^{N_M} \tag{3}$$

The average site occupation number can be written as [10]:

$$N_o = k_BT\frac{\partial \ln Z_{gc}}{\partial \mu} = N_M k_BT\frac{\partial \ln z_{gc}}{\partial \mu} \tag{4}$$

The total number of the adsorbed molecules is then written as [10,11]:

$$Q = nN_o = nN_M\frac{\left(\frac{c}{c_1}\right)^n + 2\left(\frac{c}{c_2}\right)^{2n}}{1 + \left(\frac{c}{c_1}\right)^n + \left(\frac{c}{c_2}\right)^{2n}} \tag{5}$$

The analytical expression of this model contains four

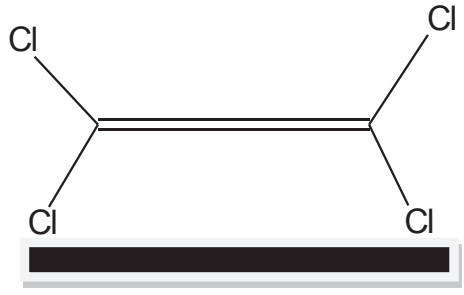

Fig. 1. Anchorage of PCE molecule by two receptor sites on activated carbon (n = 0.5).