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Adsorption of styrene sulfonate from aqueous solutions onto carbon fibers and mesoporous carbon

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ABSTRACT

The removal of styrene sulfonate from aqueous solution by using different activated carbons, microporous or mesoporous, is studied from kinetics and thermodynamics points of view. The results are interpreted in term of pore size distribution, pore organization and surface charge. Several classical models are tested both for kinetics and thermodynamics aspects. Very different behaviors are observed between the carbons but for all adsorbents, the kinetics were faster in presence of a saline solution and the amount adsorbed at saturation higher, showing the importance of surface charge that introduces an energy barrier against adsorption when molecules and surface have the same charge. Adsorption isotherms were modeled with Langmuir and double Langmuir equations and the thermodynamic parameters were calculated and correlated with the adsorption behaviors. By using adsorption calorimetry to map the adsorption site distribution, it is possible to validate or not the models.

1. Introduction

As a family of the widespread hydrophobic ionizable organic compounds, aromatic sulfonates are widely used as intermediates for the manufacturing of azo dyestuffs, pharmaceuticals, tanning agents and surfactants. In the past decades water pollution by chemical wastewater has been of increasing concern in many countries. In response to such problems, many practical techniques such as advanced oxidation, membrane filtration, biological degradation, electrochemical oxidation, photocatalytic degradation and adsorption are proposed. Among these methods, adsorption is still the most versatile and widely used, since it can effectively remove many types of pollutants and the design and operation of processes are convenient. To date, activated carbon has been known as the most popularly used adsorbent for pollutants removal. However, a number of problems associated with activated carbon such as pore blocking and slow adsorption rate inhibit its wide application. In recent years, new forms of carbon adsorbent such as activated carbon fibers (ACFs) [1–7] have been intensively developed and applied. The porous structure of ACF is mainly composed of micropores while the particulate activated carbon have often very complex structure formed by micropores, mesopores and macropores. ACFs have large external surfaces and their micropores are directly exposed on the surface, giving rise to a fast adsorption rate. These nanomaterials have been proven to possess good potential as environmental sensors or superior adsorbents for removing many kinds of organic pollutants such as volatile organic compounds [8,9], natural organic matter [10], dyes [11,12], polyaromatics hydrocarbons [13], atrazine [14], heavy metals [15,16] from an aqueous solution. In this study we use styrene sulfonate as a model substance having an aromatic structure. Styrene sulfonate and polystyrene sulfonate are also often used as natural organic matter surrogates [17–21]. The aim of this work is to study the kinetics and isotherm of adsorption of styrene sulfonate onto carbon fibers having different pore sizes and to compare the results with granular mesoporous carbon. In order to understand the adsorption processes and check the validity of classical models, the determination of the adsorption isotherms was combined to the measure of the adsorption enthalpy by microcalorimetry.

2. Materials and methods

2.1. Materials

Styrene sulfonate used as adsorbate in this study is analytical grade (Aldrich) and his main properties are given in Table 1. The size of the molecule was determined with the software Cerius2.

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Table 1
The main properties of the adsorbate.

Properties	Styrene sulfonate
Formula	$H_2C{=}CHC_6H_4SO_3Na\cdot xH_2O$
Molecular size (nm)[a]	1*0.45
Molecular weight (g mol^{-1})	206.2
pK_a (at 298 K)	1
λ_{max} in aqueous solution (nm)	255

[a] Determined with Cerius2.

Three types of carbons were used: granular mesoporous carbon (Spheron 6) and two kinds of pitch-based ACFs (A5 and A20, Ad'all Co., Japan).

2.2. Characterization of the carbons

Carbons were characterized by gas adsorption. Nitrogen sorption isotherms at 77 K where determined with an ASAP 2010 apparatus from Micromeritics for mesoporous carbon and a Quantachrome Autosorb apparatus for the fibers. The carbons were outgassed at 120 °C overnight before analysis. The BET equation was applied to determine the surface area of the mesoporous carbon. Average pore diameter and pore volume were evaluated from the nitrogen adsorption–desorption isotherms by applying the Barrett–Joyner–Halenda (BJH) model [22] for the mesoporous carbon. The BJH method is based on the Kelvin equation which defines the equilibrium pressure for capillary condensation and was applied to the desorption branch. The pore size distribution calculations for the fibers are obtained from nitrogen adsorption isotherms by applying the Quenched Solid Density Functional Theory (QSDFT) model assuming slit-shaped pores, which are typical model pores in activated microporous carbon [23]. Raman spectra were obtained using a Horiba–Jobin–Yvon HR LabRAM HR apparatus (laser wavelength: $\lambda_L = 514.5$ nm, 50× objective, numerical aperture of 0.5 leading to a laser focus diameter of 2.5 µm, resolution $\approx 1\ cm^{-1}$). The laser power was about 1 mW.

2.3. Sorption from solution

The sorption isotherms were determined by the solution depletion method. Different amounts of a stock solution of styrene sulfonate (0.01 mol L^{-1}) were introduced into glass tubes which contain 50 mg of carbon in a 20 mL aqueous solution. The solvent is either distilled water or a saline solution (0.1 mol L^{-1} NaCl). The pH of the solution was around 6.5. The tubes were stirred during the time needed to reach equilibrium. This time was determined from a preliminary kinetic study. The suspensions were then centrifuged and the concentration of styrene sulfonate was determined at the wavelength of 255 nm using a UV–vis spectrophotometer (Agilent). The specific excess amount sorbed by the carbons is given by:

$$q_e = (C_i - C_e)\frac{V}{m_s} \quad \text{in } \mu mol\ g^{-1} \tag{1}$$

where C_i and C_e are the initial and equilibrium concentrations (µmol L^{-1}), V the volume of solution (L), and m_s the mass of the solid sample (grams). All sorption isotherms were determined at 298 K.

Adsorption kinetic of styrene sulfonate ($C_i = 100$ µmol L^{-1}) was performed by analyzing the adsorption capacity at different time intervals at 298 K until the adsorption equilibrium was reached.

2.4. Microcalorimetry

Microcalorimetric measurements were carried out with a Tian–Calvet type microcalorimeter in a batch procedure [24] also called titration method. The presented results concern only those in saline solution because in water the kinetic of adsorption was too slow. The experimental conditions were the same as those of adsorption isotherms. Details concerning the experimental procedure of the calorimetric experiments were described previously [25]. Briefly, a stock solution of the molecule was injected step by step inside the microcalorimetric cell, in which the solid was maintained in suspension by a stirrer. In the reference cell, the solvent is added to the solvent. At each step, the measured heat has a contribution of both the dilution and the sorption phenomena. The dilution contribution was measured by the same procedure but without the solid inside the cell. It was subtracted from the measured heat to get the sorption enthalpy. In this study the dilution contribution is negligible. All adsorption experiments were done at 298 K.

To extract from the calorimetric results the adsorption contribution, the adsorption isotherm must be known in order to determine the amount of styrene sulfonate adsorbed during the calorimetric experiment. Therefore, the adsorption isotherms were measured under the same experimental conditions as those used for the calorimetric experiments. From the amount adsorbed and the thermal effect corrected from the dilution contribution, the differential molar enthalpy of adsorption, Δh_{ads}, was calculated and plotted as a function of coverage $\theta = q_e/q_m$ where q_m is the specific amount adsorbed at saturation.

2.5. Langmuir and Freundlich models

The adsorption isotherm equation can be derived from the chemical equilibrium between a probe molecule (P) and surface site (S) following:

$$S_{(s)} + P_{(aq)} \Leftrightarrow SP_{(s)} \tag{2}$$

where SP is the adsorbed species. Then applying the mass equation law, one obtains

$$K_L = \frac{a_{SP}}{a_S a_P} = \frac{\gamma_{x,SP} x_{SP}}{(\gamma_{x,S} x_S)(\gamma_{C,P} C_e/C^\circ)} \tag{3}$$

where a_i is the activity of the component i, γ_i is the activity coefficient, x_i is the molar fraction, C_e is the concentration of probe molecule at equilibrium (in mol L^{-1}) and C° is the reference concentration, $C^\circ = 1$ mol L^{-1}. Assuming ideal conditions both at the surface and in dilute bulk solution we may omit the term including the activity coefficients. If we additionally introduce

$$x_S = 1 - x_{SP} \tag{4}$$

the equilibrium constant becomes

$$K_L = \left(\frac{x_{SP}}{1 - x_{SP}} \frac{1}{C_e/C^\circ}\right) \tag{5}$$

The K_L value is dimensionless. The C_e value has to be taken in mol L^{-1} because $C^\circ = 1$ mol L^{-1}. C° is not written in the next part.

Rearrangement gives

$$x_{SP} = \frac{K_L C_e}{1 + K_L C_e} \tag{6}$$

The molar fraction x_{SP} can be expressed as: