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Competitive Adsorption of *p*-Hydroxybenzoic Acid and Phenol on Activated Carbon: Experimental Study and Modeling

Caroline Andriantsiferana¹; Carine Julcour-Lebigue²; Carmen Creanga-Manole, Ph.D.³; Henri Delmas⁴; and Anne-Marie Wilhelm⁵

Abstract: The competitive adsorption of phenol and *p*-hydroxybenzoic acid (4HBA) has been investigated on activated carbon (AC) for a wide range of concentrations under unbuffered conditions. The results show a preferential adsorption of 4HBA, which can be explained by the lower solubility of 4HBA and the electrostatic interactions between the AC and the ionic form of the molecule in this range of pH. The Langmuir isotherm was found suitable to describe the single-component adsorptions, indicating a monolayer adsorption in accordance with the microporous nature of the AC. Then the empirical extended Langmuir model and the predictive ideal adsorption solution theory model have been compared for competitive adsorption. When using parameter values optimized for single pollutants, both models show rather poor agreement with mixture data. However, after fitting the extended Langmuir parameters with the whole data set, better results can be obtained, showing that there is some peculiar behavior of the mixture under oxic conditions, probably tied to the effect of 4HBA on the irreversible adsorption of phenol. DOI: 10.1061/(ASCE)EE.1943-7870.0000600.

CE Database subject headings: Phenol; Adsorption; Activated carbon; Experimentation.

Author keywords: Phenols; Irreversible adsorption; Extended Langmuir model; Ideal adsorption solution theory.

Introduction

Phenols are considered as priority pollutants because they are harmful to organisms even at low concentrations (Green et al. 1988; Petroustos et al. 2007). The sources of phenol pollution in the aquatic environment are wastewaters from paint, pesticide, polymer, petroleum, and other chemical industries. Various alternative technologies to biological degradation are available to remove those molecules from wastewater: physical processes such as distillation (Tumakaka et al. 2007), solvent extraction (Pinto et al. 2005), membrane separation (Xiao et al. 2006), and adsorption (Dabrowski et al. 2005), as well as chemical oxidation with various oxidants: ozonation (Merle et al. 2010), catalytic wet air oxidation (Stüber et al. 2005; Levec and Pintar 2007), or photocatalysis (Chong et al. 2010). Although these oxidation techniques can efficiently destroy phenolic pollutants, they involve high costs owing to the use of chemicals, catalysts, and/or high temperature and pressure (Busca et al. 2008). Therefore, adsorption onto activated carbon (AC) is usually considered as an efficient and cost-effective

process for the removal of such organic compounds in dilute aqueous solutions (Kilduff and King 1997). Indeed, many studies have proved the high affinity of AC for these aromatics and the literature provides different theories to explain this strong interaction (Terzyk 2003; Dabrowski et al. 2005). Coughlin and Ezra (1968) have proposed that the adsorption of phenols onto the surface of AC is governed by the dispersion interactions between the aromatic ring of phenol and the electron-rich structure of the AC graphene layers. Thus, the nature of functional groups situated at the edges of the AC basal planes or found as substituents of the aromatic solute strongly influences the adsorption properties. In this mechanism, the presence of electron-withdrawing groups on the carbon surface, such as acidic oxygen groups (carboxyl and hydroxyl functionalities), inhibits the adsorption of phenols by reducing the electron density of the basal plane. In contrast, the presence of electron-withdrawing substituents on the molecule improves the adsorption capacity of the carbon by reinforcing the π - π interaction. Mattson et al. (1969) have suggested another mechanism to be predominant, based on the formation of donor-acceptor complexes between the aromatic ring of the adsorbate and the carbonyl groups at the surface of AC. In addition to these mechanisms, the solvent effect is often mentioned. Both phenolic compounds and water molecules can compete with carbon surface and the formation of H bonds with surface carboxyl groups can result in a lower uptake of the organic compounds (Moreno-Castilla 2004). Moreover, other authors have shown that irreversible adsorption also takes place, leading to the formation of phenol oligomers by oxidative coupling on the carbon surface (Snoeyink et al. 1969; Magne and Walker 1986; Grant and King 1990). Pimenta and Kilduff (2006) have reported that this reaction alone cannot explain irreversible phenol adsorption. Terzyk (2003) has suggested that phenol molecules react with active sites of the AC, which can result in a covalent bonding to the surface. An additional phenomenon to be accounted for is the electrostatic interaction or repulsion between the carbon and the adsorbates. The

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surface charge of the activated carbon and the ionic state of phenols depend on the pH of the solution. Consequently, the pH value above which the total surface of the carbon is negatively charged, called the point of zero charge (pH_{PZC}), and the pK_a of the molecules have a great influence (Dabrowski et al. 2005). Considering the complex nature of all these different interactions, a lot of parameters have to be examined to understand competition phenomena when several molecules are present: their molecular size and solubility (Singh and Yenkie 2006), their hydrophobicity when aqueous solutions are involved (Monneyron et al. 2002), their ability for dissociation, whether oxic or anoxic conditions are used (Abuzald and Nakhla 1994; Terzyk 2007), and the electronic properties of the different substituents for aromatic derivatives (Nouri and Haghseresht 2004).

A number of models are available that can be used to model single-solute adsorption systems. They can be classified into the following categories: simple isotherm models for homogeneous surfaces without lateral interactions, such as Langmuir and Jovanovic equations; isotherm models for heterogeneous surfaces without lateral interactions, such as Freundlich equation; other empirical isotherm models, such as Langmuir–Freundlich, Fowler–Guggenheim, Radke–Prausnitz, Redlich–Peterson, Khan, and Tóth isotherms (Quinones and Guiochon 1996; Garcíá-Galdo and Jáuregui-Haza 2001). In addition to being thermodynamically inconsistent, the latter models may also require additional parameters that make their application to solute mixtures difficult. Thus, to describe competitive adsorption, the most commonly used model is the extended Langmuir model (EL), which usually performs rather well (Haghseresht et al. 2003). However, this model is not based on fundamental theories contrary to the predictive ideal adsorption solution theory (IAST) (Myers and Prausnitz 1965). IAST assumes the adsorbed phase to behave like an ideal solution of the adsorbed molecules. According to some authors, IAST gives satisfactory results for the competitive adsorption of some phenolic compounds (Monneyron et al. 2002). Model adequacy depends on the quality of the fit of single-component parameters especially in the low concentrations range (Baudu et al. 1989; Choy et al. 2004). Discrepancies between experimental data and values predicted by IAST have been attributed to additional effects that are not accounted for by this model: influence of the pH, ionic dissociation effect, oligomerization under oxic conditions (Lu and Sorial 2009), or nonideal behavior of the adsorbed phase (Radke and Prausnitz 1972).

The objective of this study was to investigate the adsorption of two aromatic molecules representative of industrial wastewaters: phenol and *p*-hydroxybenzoic acid (4HBA). 4HBA is a biorecalcitrant pollutant released during the production of olive oil

(Mantzavinos and Kalogerakis 2005). It is also an intermediate product of phenol oxidation over AC (Stüber et al. 2005). Adsorption onto AC could be proposed to remove such refractory compounds either by pretreatment or posttreatment methods as needed.

Single-component and mixture equilibrium data have been obtained for a wide range of concentrations. For single-component adsorption, classic Langmuir and Freundlich models have been compared to represent the isotherms. Then extended models and IAST equations are tested to describe the competitive adsorption of these solutes.

Materials and Methods

Adsorbates

The two phenolic compounds used in this study, phenol and 4HBA, have been supplied with purities equal to 98.5 and 99%, respectively (Sigma-Aldrich). Different initial solutions have been prepared according to the solubility of the two molecules (cf. Table 1). For single-solute studies, initial concentrations of phenol and 4HBA ranged from 5–100 mol m⁻³ and from 3–30 mol m⁻³, respectively. For mixture studies, the total initial concentration ranged between 4 and 63 mol m⁻³ and three different molar percentages (phenol/4HBA) are used: 30/70, 50/50, and 70/30.

Adsorbent

- Physical properties: A commercial AC, produced from wood, has been used in this study (Merck, Ref. No. 1.02514.1000). Its physical properties are given in Table 2. The textural characterization is deduced from nitrogen adsorption at 77 K using an ASAP 2010M apparatus (Micromeritics, Norcross, Georgia). The specific surface area is determined from the Brunauer, Emmett, and Teller method (commonly referred as BET method) for relative pressure range (p/p_0) of 0.01–0.2 (Brunauer et al. 1938).

Methods from Horvath and Kawazoe (1983) and Barrett et al. (1951), referred as HK and BJH, respectively, are used to assess the micropore and mesopore volumes, respectively. The mean pore diameter is deduced from the total porous volume at $p/p_0 = 0.98$ and the BET surface area.

The true density is measured by helium pycnometry (AccuPyc 1330TC equipment supplied by Micromeritics).

- Acidic and basic surface groups: The amounts of acidic and basic surface groups (Table 3) have been measured according to

Table 1. Selected Properties of the Phenolic Compounds

| Adsorbate | MW (g) | pK_{a1}/pK_{a2} | Solubility at 25°C (mol m ⁻³) | $\log K_{ow}$ ^a | Critical oxidation potential (V) |
|-----------|--------|-------------------|-------------------------------------------|----------------------------|----------------------------------|
| 4HBA | 138.1 | 4.58/9.23 | 36 | 1.37 | 1.36 |
| P | 94.1 | 9.89 | 1,010 | 1.51 | 1.089 |

Note: 4HBA = *p*-hydroxybenzoic acid; MW = molecular weight; P = phenol.

^aLog octanol–water partitioning coefficient.

Table 2. Textural Properties of the Activated Carbon Merck 2514

| d_{43} (mm) | True density (g L ⁻¹) | Apparent density (g L ⁻¹) | Total porous volume ^a (cm ³ g ⁻¹) | Microporous volume ^b (cm ³ g ⁻¹) | Mesoporous volume ^c (cm ³ g ⁻¹) | BET-specific surface (m ² g ⁻¹) | Average pore diameter (Å) |
|---------------|-----------------------------------|---------------------------------------|---------------------------------------------------------------------|--------------------------------------------------------------------|-------------------------------------------------------------------|--------------------------------------------------------|---------------------------|
| 0.3 | 2,500 | 1,032 | 0.53 | 0.37 | 0.20 | 980 | 22 |

Note: BJH = Barrett–Joyner–Halenda; HK = Horvath–Kawazoe method.

^aMeasured at $p/p_0 = 0.98$.

^bObtained from the HK method.

^cObtained from the BJH method.

Table 3. Surface Groups of the MERCK Activated Carbon (Boehm Titration) and pH_{PZC}

| Surface groups ($\text{mmol g}_{\text{AC}}^{-1}$) | | | | | |
|-----------------------------------------------------|---------|--------|--------------|-------------|--------------------------|
| Carboxyl | Lactone | Phenol | Total acidic | Total basic | pH_{PZC} |
| 0.035 | 0.015 | 0.16 | 0.21 | 0.46 | 8.9 |

Note: $\text{pH}_{\text{PZC}} = \text{pH}$ at the point of zero charge.

the Boehm method (Boehm 1966). Approximately 1 g of AC is introduced in vials containing 20 mL of each of the following 0.1 N aqueous solutions: NaHCO_3 , Na_2CO_3 , NaOH , and HCl . The vials are degassed under N_2 , closed, and stirred for 24 h. Then, the solutions are filtered and an aliquot of 10 mL is titrated with 0.1 N HCl or NaOH (DL50; METTLER TOLEDO). The method is based on the following assumptions: NaHCO_3 neutralizes carboxyl groups only, Na_2CO_3 reacts with both carboxyl and lactone groups, while NaOH is assumed to neutralize all acidic surface groups. The number of basic sites is calculated from the amount of HCl that has reacted with the carbon. Triplicate titrations are carried out in each case.

The acido-basicity of the adsorbent is also assessed from the determination of pH_{PZC} , measured by the so-called pH drift method (Lopez-Ramon et al. 1999).

Dynamic and Isotherm Studies

To perform the adsorption studies, the original AC (in the form of 1.5 mm pellets) is crushed and sieved. The volume mean diameter d_{43} of the carbon used in this study is 0.3 mm.

Dynamic experiments are performed in a stirred reactor filled with 300 mL of pollutant solution (concentration: 7.49 mol m^{-3} of each pollutant) containing 1.5 g of AC. At regular intervals of time, an aliquot of 1 mL is withdrawn—in the limit of 15 samples (5% of the volume). The samples are filtered using $0.25 \mu\text{m}$ nylon filter membranes before analysis (see the “Analytical Methods” section).

For equilibrium studies, 100 mL of solution and 0.5 g of AC are mixed and allowed to react in a stirred flask for 12 h, which is long enough to attain equilibrium (see the “Adsorption Dynamics” section). Then, a sample of the solution is taken, filtered, and analyzed. The amount of adsorbed pollutant at equilibrium is calculated from initial and final concentrations in the liquid phase. Some experiments have been duplicated or triplicated showing less than 5% difference. As the solutions are not buffered, the final pH varies, being in the range of 4–5 for both phenol and mixture solutions. For 4HBA solutions, the pH ranges between 3.5 and 5. All the adsorption experiments are carried out at room temperature ($22 \pm 1^\circ\text{C}$) using a thermostated bath.

Analytical Methods

For single-solute adsorption, the analysis of liquid samples has been carried out using a spectrophotometer (Spectronic GENESYS 2; Thermo Electron, Madison, Wisconsin), which was set at a wavelength of 270 nm. For multisolute adsorption, an HPLC system has been used, including a P1000XR pump equipped with a degasser and a UV2000 dual wavelength UV detector (Thermo Finnigan, San José, California). The separation is achieved using a C18 reversed-phase column (ProntoSIL 120-5-C18-AQ; 250 mm length \times 4 mm i.d., $5 \mu\text{m}$ particle size) with a mobile phase containing acidified water ($\text{pH} = 2.2$) and acetonitrile (30%), fed at 1 mL min^{-1} . The detector wavelength is set to 254 nm and the temperature of the column is maintained at 30°C .

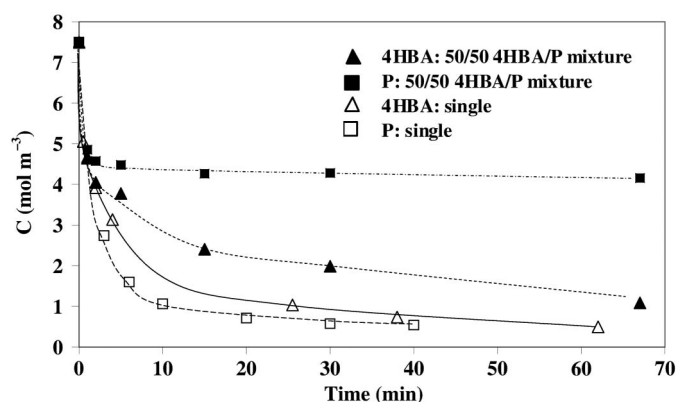


Fig. 1. Adsorption kinetics of 4HBA and phenol (P) on 0.3-mm AC (initial concentration = 7.49 mol m^{-3} of each pollutant, $w_{\text{AC}} = 1.5 \text{ g}$, $V_L = 300 \text{ mL}$)

Results and Discussion

Adsorption Dynamics

Dynamic experiments are used to assess the time required for attaining equilibrium. In single-solute conditions, the shape of concentration–time profiles obtained with phenol and 4HBA is rather similar as shown in Fig. 1. The equilibrium is attained within approximately 1 h for both molecules, a little faster for phenol owing to its higher molecular diffusivity in water ($D_{m,P} = 9.3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ and $D_{m,4\text{HBA}} = 7.9 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$).

In binary solution, the difference between the adsorption dynamics of the two molecules is amplified, as the equilibrium is attained more rapidly for phenol (less than 20 min), but requires more than 1 h for 4HBA. This might be due to competition effect between the two molecules, phenol being much less adsorbed in the presence of 4HBA.

Single-Solute Isotherms: Freundlich and Langmuir Models

Among the many existing isotherm models, the Freundlich and Langmuir equations are the most widely used models due to their simplicity (Do 1998). Fig. 2 compares the experimental and

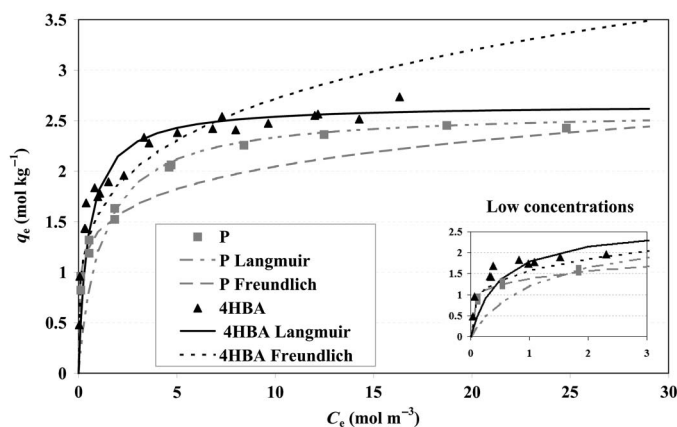


Fig. 2. Single-solute adsorption: experimental and fitted isotherms of 4HBA ($3.5 < \text{pH} < 5$) and phenol (P) ($4 < \text{pH} < 5$) on Merck activated carbon at 22°C

Table 4. Parameters of Langmuir and Freundlich Models Determined from Single-Solute Adsorption Experiments at 22°C

| Adsorbate | Langmuir model $q_{e,i}^0 = K_{L,i}q_{m,i}C_{e,i}^0/(1 + K_{L,i}C_{e,i}^0)$ | | | Freundlich model $q_{e,i}^0 = K_{F,i}(C_{e,i}^0)^{1/n_i}$ | | |
|-----------|-----------------------------------------------------------------------------|-----------------------------------------------|-------|-----------------------------------------------------------|-------------------------------------------------------------------------------------------------------------|-------|
| | $q_{m,i}$ (mol kg _{AC} ⁻¹) | $K_{L,i}$ (m ³ mol ⁻¹) | R^2 | $1/n_i$ | $K_{F,i}$ mol kg _{AC} ⁻¹ (m ³ mol ⁻¹) ^{1/n_i} | R^2 |
| 4HBA | 2.66 | 2.091 | 0.997 | 0.236 | 1.578 | 0.863 |
| Phenol | 2.60 | 0.878 | 0.998 | 0.166 | 1.394 | 0.938 |

Note: 4HBA = *p*-hydroxybenzoic acid.

modeled adsorption isotherms of phenol and 4HBA. The two phenolic compounds exhibit the same isotherm shape, corresponding to the type I of International Union of Pure Applied Chemistry classification. Calculation of isotherm parameters has been performed using linearization of the corresponding equations. The Langmuir equation is found to be the most suitable model for both molecules, except at very low concentrations. The concentration range is indeed too wide to select a model that fits the whole experimental data. The Langmuir parameters are given in Table 4 showing a slightly higher value of the monolayer capacity $q_{m,i}$ for 4HBA. These saturation capacities lie within the range of reported values for AC and phenolic compounds, between 2 and 3 mol kg_{AC}⁻¹ under ambient temperature and unbuffered conditions (Laszlo et al. 2006; Kumar et al. 2007; Liu et al. 2010). The high adsorptive performance of the Merck AC is due to its microporosity and basic character (see Table 3). The values of $K_{L,i}$ for the two phenols show a stronger interaction between 4HBA and AC. A first explanation can be found in the lower solubility of 4HBA (cf. Table 1), which is often associated to a better uptake (Garcia-Araya et al. 2003). An additional parameter is the existence of electrostatic interactions between the ionic form of 4HBA and the AC. For pH ranging between 3.5 and 5, phenol stays in a nonionic form, while 4HBA ($pK_{a1} = 4.6$) is partially dissociated. As the pH of the solution is also lower than the pH_{PZC} of the Merck AC ($pH_{PZC} = 8.9$), the carbon surface is positively charged (Dabrowski et al. 2005) and thus attracts the *p*-hydroxybenzoate anions preferentially. As stated in the “Introduction” section, further parameters are also proposed to explain the different adsorption behaviors of the phenols, namely the hydrophobicity of the molecules and the electronic properties of the aromatic ring substituents (through π - π interactions). Values of $\log K_{ow}$ reported in Table 1 indicate a favorable adsorption of phenol because it is more hydrophobic than 4HBA. The influence of this parameter seems thus to be low because an opposite behavior is observed. Finally, the electron-withdrawing character of -COOH group could have a favorable effect on the adsorption of 4HBA in agreement with the present results (Coughlin and Ezra 1968).

Binary Competitive Adsorption: EL Model and IAST

- Experimental equilibrium data: Fig. 3 shows the experimental equilibrium data obtained starting from different initial proportions of phenol and 4HBA ($4 < pH < 5$, $T = 22^\circ C$). It should be noticed that a given experiment results in two different final concentrations. In each case, the $q_e = f(C_e)$ curve of 4HBA exhibits a classic shape (type I), while that of phenol shows a maximum at very low concentration.

When starting with an excess of 4HBA (70% in mole), the concentrations of phenol and 4HBA reach similar values in the final mixture. However, when starting with either an excess of phenol (70% in mole) or an equimolar solution, phenol is more concentrated in the final solution. The binary adsorption data thus reinforce the previous conclusion of a better adsorption of 4HBA, which clearly applies here whatever the initial proportions of the two compounds are.

The cumulated equilibrium data in Fig. 3 correspond to the total amount of adsorbed molecules as a function of the total concentration (phenol + 4HBA). When phenol is predominant, the total amount of adsorbed molecules lies below the single-solute isotherms, while an intermediate behavior could be expected. In a single-solute system and under oxic conditions, phenol gets oligomerized over AC due to its low critical oxidation potential value, unlike 4HBA (Table 1). This oligomerization results in an irreversible adsorption in addition to the physical one observed under anoxic conditions (Lu and Sorial 2007, 2009). According to the results of these authors for phenol/2-ethylphenol and 2-methylphenol/2-nitrophenol systems, the presence of a poorly oligomerizable molecule (2-ethylphenol or 2-nitrophenol) seems to hinder the oligomerization of the other (phenol or 2-methylphenol) as an overlapping of oxic and anoxic isotherms is observed for the mixtures. This might also be the case for the present binary system, wherein the presence of 4HBA may prevent the oligomerization of phenol, and thus explaining the lower adsorption of the mixture.

- EL model: This model gives the amount of the adsorbed component *i* in the presence of other adsorbed components as follows:

$$q_{e,i} = \frac{q_{m,i} \times K_{L,i} \times C_{e,i}}{1 + \sum_{j=1}^m K_{L,j} \times C_{e,j}} \quad (1)$$

where $q_{e,i}$ = amount of component *i* adsorbed per unit weight of adsorbent, $C_{e,i}$ = equilibrium concentration of the component *i* in the multicomponent solution, and m = the number of adsorbed species.

This model assumes that the adsorbates compete for the same binding sites and that there is no interaction between adsorbed species. Its thermodynamic consistency requires the monolayer capacity of the molecules to be the same (Do 1998),

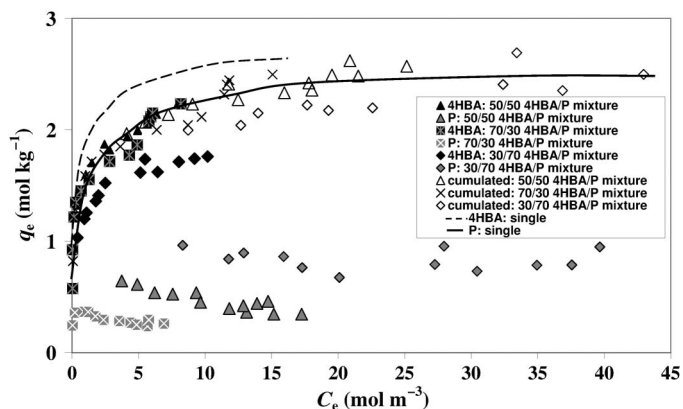


Fig. 3. Binary competitive adsorption: experimental equilibrium data obtained when using different initial concentrations of 4HBA and phenol (P) ($4 < pH < 5$, $T = 22^\circ C$). The cumulated data correspond to the total amount of adsorbed molecules as a function of the total concentration (P+4HBA). The lines correspond to the single component isotherms of 4HBA and P

Table 5. Parameters of Binary Langmuir Adsorption Models at 22°C along with 95% Confidence Intervals—in Parentheses—for OEL and Respective MRE

| Model | Parameters | Values | MRE (%) |
|-----------------------------------------------|----------------------------------------------------|----------------|-------------------|
| EL model derived from single-solute isotherms | $q_{m,4HBA}$ (mol kg _{AC} ⁻¹) | 2.66 | 71.7 |
| | $q_{m,P}$ (mol kg _{AC} ⁻¹) | 2.60 | |
| | $K_{L,4HBA}$ (m ³ mol ⁻¹) | 2.091 | |
| | $K_{L,P}$ (m ³ mol ⁻¹) | 0.878 | |
| OEL model | $q_{m,4HBA}$ (mol kg _{AC} ⁻¹) | 2.25 (±0.17) | 17.2 ^a |
| | $q_{m,P}$ (mol kg _{AC} ⁻¹) | 2.49 (±0.35) | |
| | $K_{L,4HBA}$ (m ³ mol ⁻¹) | 9.118 (±2.610) | |
| | $K_{L,P}$ (m ³ mol ⁻¹) | 0.660 (±0.222) | |

Note: EL = extended Langmuir; MRE = mean relative error; OEL = optimized extended Langmuir; MRE is calculated as $MRE(\%) = (100/2n) \sum_{j=1}^{2n} |(q_{e,j}^{\text{exp}} - q_{e,j}^{\text{calculated}})/q_{e,j}^{\text{exp}}|$.

^aOEL model represents 90% of the data with a relative error of less than 40%.

which is nearly the case for the two phenols investigated ($q_{m,4HBA} = 2.66 \text{ mol kg}_{AC}^{-1} \sim q_{m,P} = 2.60 \text{ mol kg}_{AC}^{-1}$).

The parameters $K_{L,i}$ and $q_{m,i}$ used for modeling binary adsorption system are theoretically those calculated for single components. As this representation most often fails, especially when the values of $q_{m,i}$ are different, some authors have proposed a modified version of this model by considering its parameters as adjustable ones (Baudu et al. 1989; Chern and Chien 2003). In the present case, the parameter values of this optimized EL (OEL) model have been obtained from a nonlinear regression using the generalized reduced gradient method with the whole experimental data (single solutes and mixtures) and a convergence criterion based on the sum of the square relative error between modeled and experimental values of adsorbed amounts. Table 5 shows that the original EL model is not suitable to describe the binary adsorption, with very large relative errors for some of the $q_{e,i}$ values. However, after fitting the parameters $K_{L,i}$ and $q_{m,i}$ with the whole data set, a satisfactory agreement can be obtained with such a model (cf. Fig. 4). Fig. 4 shows the simulations of EL model derived from single-solute isotherms (dotted lines) and OEL model (small symbols) after fitting the parameters with the whole data set for a binary competitive adsorption. It should be noticed that the change in parameters concerns much more $K_{L,i}$ than $q_{m,i}$. $K_{L,4HBA}$ should be strongly increased as compared with the value previously obtained when fitting the single-component equilibrium data, and is much greater than $K_{L,P}$, which is in agreement with the strong preferential adsorption of 4HBA. As previously reported in the “Single-Solute Isotherms: Freundlich and Langmuir Models” section, the value of the Langmuir parameter $K_{L,4HBA}$ is too small to model 4HBA adsorption correctly at very low concentrations. This inadequacy could also explain the greater optimized value of $K_{L,4HBA}$. Conversely, the optimization of $K_{L,P}$ with mixture data results in a lower value of this parameter: the presence of 4HBA clearly hinders the adsorption of phenol. Only a decrease of phenol oligomerization could explain this smaller value of $K_{L,P}$ in mixture.

- IAST: Myers and Prausnitz (1965) developed the IAST for gas–solid system, which was later extended to liquid–solid adsorption system (Radke and Prausnitz 1972). This theory aims to predict the multisolute adsorption using the data for single-solute adsorption. To reduce the complexity of the computer program, the single-solute isotherms used are classically the Langmuir or Freundlich models. The IAST model relies on the following hypotheses and equations (Cheung et al. 2003). Defining the molar fraction of adsorbate i

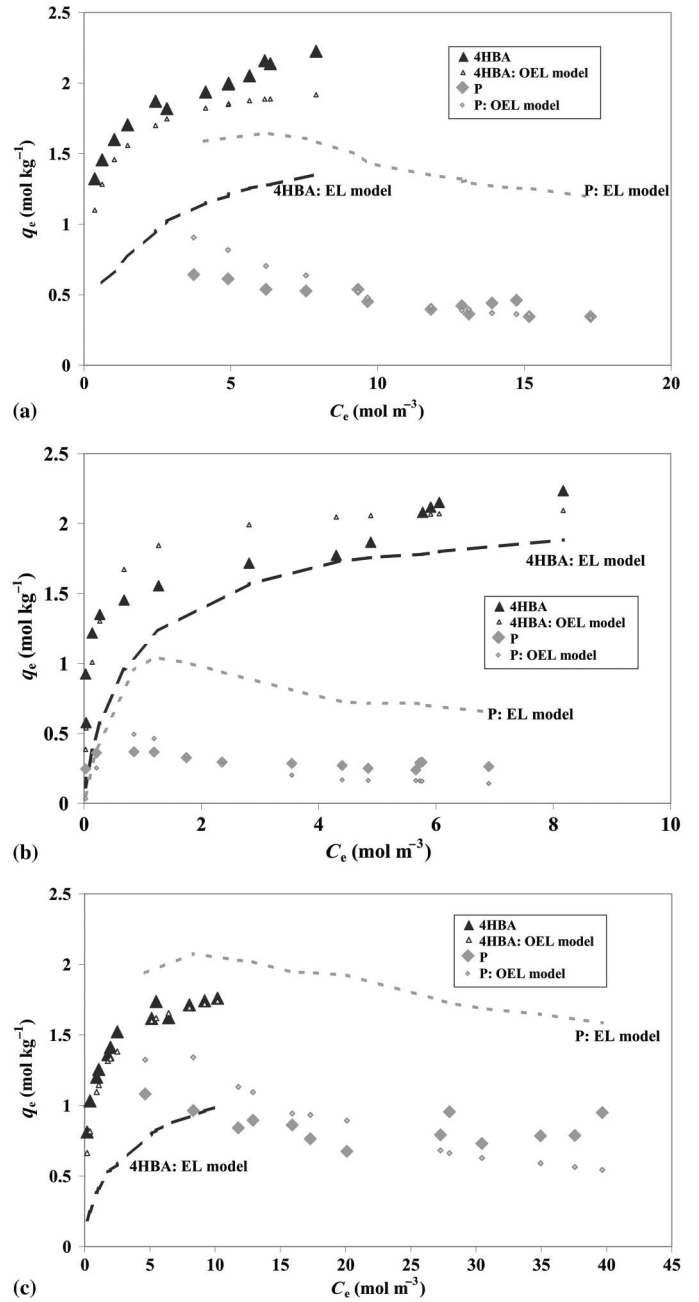


Fig. 4. Binary competitive adsorption; simulations of extended langmuir model derived from single solute isotherms (EL, lines) and optimized extended langmuir model (OEL, small symbols) after fitting the parameters with the whole data set: (a) $C_{0,P} = C_{0,4HBA} = 0.5C_{0,\text{total}}$; (b) $C_{0,4HBA} = 0.7C_{0,\text{total}}$ and $C_{0,P} = 0.3C_{0,\text{total}}$; (c) $C_{0,4HBA} = 0.3C_{0,\text{total}}$ and $C_{0,P} = 0.7C_{0,\text{total}}$

$$s_i = \frac{q_{e,i}}{q_T} \quad (2)$$

with q_T = total molar solid-phase concentration on the adsorbent, the following equation stands for the solid phase:

$$\sum_{i=1}^n s_i = 1 \quad (3)$$

All the components of the mixture behave like ideal adsorbed solutes. The reference state is chosen so that the spreading pressure exerted by the adsorbed solutes on the solid surface is the

same for the mixture (π_m) as for its individual component when single (π_i^0) as follows:

$$\pi_1^0 = \pi_2^0 = \dots = \pi_n^0 = \pi_m \quad (4)$$

The adsorbed phase can be considered as an ideal solution of the adsorbed components so that at equilibrium the concentration of each component in the liquid phase ($C_{e,i}$) is proportional to its molar fraction in adsorbed phase (s_i) as follows:

$$C_{e,i} = s_i \times C_{e,i}^0 \quad (5)$$

where $C_{e,i}^0$ = liquid-phase reference concentration for the single-solute system that has identical temperature and spreading pressure as the mixture.

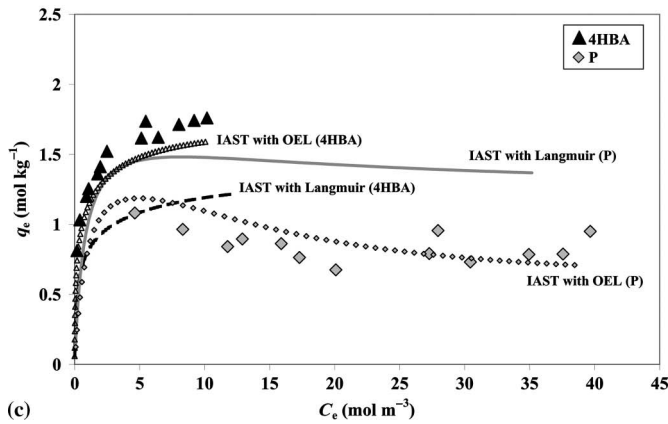
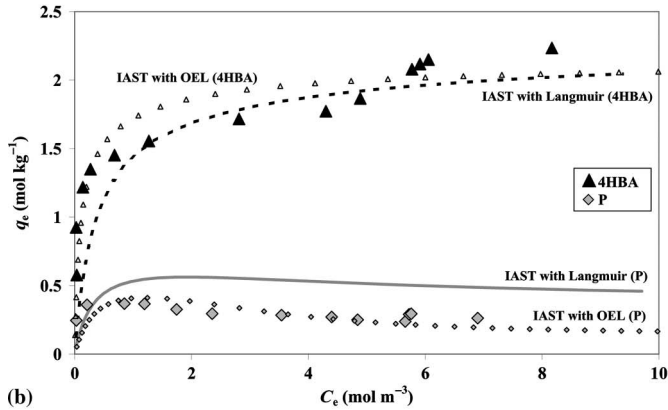
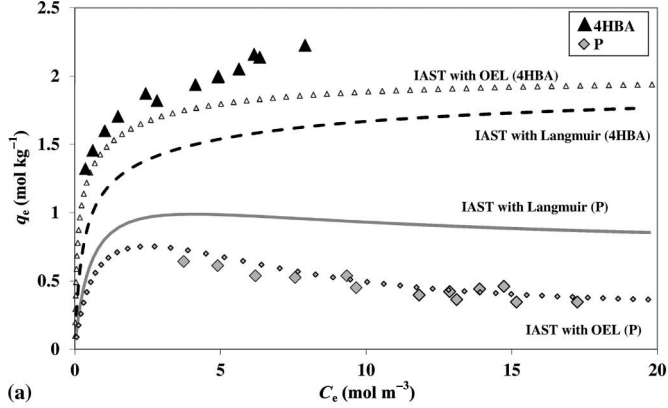


Fig. 5. Binary mixture adsorption; simulations of IAST when using parameter values of single solute Langmuir isotherms (Langmuir, lines) and those of Optimized Extended Langmuir model (OEL, small symbols): (a) $C_{0,P} = C_{0,4HBA} = 0.5C_{0,total}$; (b) $C_{0,4HBA} = 0.7C_{0,total}$ and $C_{0,P} = 0.3C_{0,total}$; (c) $C_{0,4HBA} = 0.3C_{0,total}$ and $C_{0,P} = 0.7C_{0,total}$

For the Langmuir model, the reduced spreading pressure Π_i^0 can be calculated by Eq. (6)

$$\Pi_i^0 = \frac{\pi_i^0 \times A}{R \times T} = \int_0^{C_{e,i}^0} \frac{q_{e,i}^0}{C_{e,i}^0} dC_{e,i}^0 = q_{m,i} \ln(1 + K_{L,i} C_{e,i}^0) \quad (6)$$

where A = surface area of the solid, $q_{e,i}^0$ = concentration of adsorbate i in equilibrium with $C_{e,i}^0$.

This equation can thus take the form

$$C_{e,i}^0 = \frac{\exp(\Pi_m/q_{m,i}) - 1}{K_{L,i}} \quad (7)$$

The last equations to consider for IAST are the following:

$$q_T = \left(\sum_{j=1}^n \frac{s_j}{q_{e,j}^0} \right)^{-1} \quad (\text{ideal adsorbed solution}) \quad (8)$$

and the mass balance for each component i

$$C_{0,i} = C_{e,i} + \frac{w_{AC}}{V_L} q_{e,i} \quad (9)$$

with w_{AC} = weight of AC, V_L = volume of solution, $C_{0,i}$ = the initial liquid-phase concentration of component i .

Combining Eqs. (2), (5), (8), and (9) gives

$$C_{0,i} = \left[C_{e,i}^0 + \frac{w_{AC}}{V_L} \left(\sum_{j=1}^n \frac{s_j}{q_{e,j}^0} \right)^{-1} \right] s_i \quad (10)$$

For given values of $C_{0,i}$, the values of $C_{e,i}^0$, Π_m , and s_i are calculated by solving simultaneously Eqs. (3), (7), and (10) with MATLAB solver (fsolve function).

IAST is based on a fundamental theory and the results obtained are generally in good agreement with experimental data if the solutes show similar chemical characteristics and no interaction (Monneyron et al. 2002).

Fig. 5 shows the simulations of IAST when using parameter values of single-solute Langmuir isotherms (line for P; dotted line for 4HBA) and those of OEL model (small symbols) for a binary mixture adsorption. As observed previously for the extended Langmuir model, using Langmuir parameters optimized from single component data, a poor agreement is obtained between the predicted and experimental values of $q_{e,i}$, especially when 4HBA is in default [Fig. 5(c)]. Using optimized parameters of the Extended Langmuir model (OEL) results in a much better prediction, proving an interaction between the molecules (effect of 4HBA on the oligomerization of phenol).

Conclusions

The main conclusions of this work are the following:

- In single-solute aqueous solution, the affinity of 4HBA for AC is higher than that of phenol. This trend is linked to the weak solubility of 4HBA as compared to phenol, to the partial dissociation of 4HBA in the investigated range of pH (electrostatic interaction with positively charged carbon surface), and to the favorable effect of the electron-withdrawing character of the $-\text{COOH}$ group.

- In competitive adsorption, the preferential adsorption of 4HBA is much higher than expected from single adsorption data and is observed even when phenol is in excess. EL and IAST models based on single-solute data fail to predict this competitive adsorption.
- EL model optimized on the whole data set including mixtures (OEL) gives a much better prediction (mean relative error of 17.2% compared to 71.7% with EL using single-solute parameters). Similarly, IAST model fit is significantly improved by using OEL parameters.
- Such deviation from ideal behavior might be related to irreversible adsorption effects, as already reported by Lu and Sorial (2007, 2009). In this case, the presence of 4HBA is thought to hamper the oligomerization of phenol.

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