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On the mechanism of benzene and toluene adsorption in single-compound and binary systems: energetic interactions and competitive effects

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ABSTRACT

This work reports an experimental and modelling analysis of benzene/toluene adsorption from model groundwater on a commercial activated carbon in single-compound and binary systems. Single-compound results show that toluene is more adsorbed than benzene and an increase in its adsorption capacity gives rise to lateral interactions between the adsorbed molecules. This is likely to be due to the presence of electron-donor methyl groups in the toluene molecule, which determines an increase in the electronegativity of the aromatic ring and, consequently, stronger attractions with the nucleophilic basal plane of activated carbon. Binary results indicate that toluene has the highest adsorption capacity, but some competitive effects arise for both the analytes. A modelling analysis of the binary system shows that the ideal adsorbed solution theory model can provide a very good prediction of adsorption data for both compounds, over the whole range of concentration investigated.

Keywords: Groundwater; Benzene; Toluene; Competitive adsorption; Ideal adsorbed solution theory

1. Introduction

Organic micropollutants, such as benzene and toluene, are typical groundwater contaminants and their occurrence is mainly due to accidental leakages and illegal discharges of gasoline or petrol derivatives [1]. These compounds are toxic and benzene, in particular, is formally recognized as carcinogenic [2]. Accordingly, maximum concentration levels in groundwater are established worldwide; for example, the Italian regulatory limits are set at 1 and 15 μg/L for benzene and toluene, respectively.

The removal of these compounds from polluted groundwater is a necessary task and adsorption is a widely adopted remediation technique. Adsorption can be applied as ex situ treatment, for example, as a part of the pump and treat technique, or as in situ treatment, as in permeable reactive barriers filled with adsorbents [3,4]. In all its multiple and diverse applications, adsorption has proven to be a reliable technology, characterized by good efficiency and great versatility that make it suitable to be applied also when a multiple contamination occurs [5–7]. In the last years, many experimental works have investigated the suitability of different sorbents – both commercial [8–10] and low-cost materials [11–13] – for the capture of benzene and its derivatives, and activated carbon (AC) appears as the most frequently used, sometimes in the form of fibres [14] or nanotubes [15,16].

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Despite the large industrial application of this technology, the study of the dynamics of single and multicomponent adsorption of specific compounds on AC surface has received limited attention, while extensive research has focused on the adsorption phenomenology, in the past decades. Since the latest scientific guidelines list adsorption among the best available techniques for groundwater depuration, there is a renewed interest in a critical study of the adsorption phenomena, focused on each single adsorbate having its peculiar adsorption properties.

Adsorption on AC is highly dependent on sorbent properties, both physical (e.g., microporosity) and chemical (e.g., surface chemical groups) [15]. On the other side, the thermodynamic parameters of water, such as pH and temperature, have a significant influence on solid performances. Focusing on aromatic compounds in their molecular form (i.e., when solution pH << pKa), it is commonly believed that a high concentration of acidic oxygen containing surface groups is highly detrimental to adsorption – because of a preferential water adsorption – independently of adsorbate polarity [17,18]. On the contrary, a high micropore volume enhances the adsorption of aromatic compounds, even if steric hindrance phenomena might occur [19,20]. However, the influence of molecule structure, in particular of the substituent functional group, on any aromatic ring present, should also be taken into account to assess the dynamics of adsorption of specific aromatic compounds. In addition, a thorough modelling analysis accounting for the effect of the main operating parameters is an invaluable tool for the design and optimization of an adsorption system devoted to the removal of pollutants from water. Hence, this work aims at analyzing the mechanism of the adsorption of benzene and toluene in model groundwater on a commercial granular activated carbon (GAC) and their influence on competitive adsorption.

Experimental tests were carried out in both single-compound and binary systems, varying some of the main thermodynamic parameters (i.e., concentration and temperature). A thermodynamic analysis was carried out in order to assess the energetic interactions between the two adsorbates and GAC surface, so as to address the differences in their adsorption capacity. Finally, a modelling analysis of both single-compound and binary data was carried out based on the ideal adsorbed solution theory (IAST).

2. Materials and methods

The AC used in this research work (Filtrasorb 400, F400, from Calgon Carbon Corporation, Pittsburgh, USA) is mainly microporous (micropore volume equal to 0.33 cm^3/g) and has a Brunauer–Emmett–Teller surface area approximately equal to 900 m^2/g. The surface is slightly basic, being $pH_{pzc} = 8$. This material has a narrow particle size distribution; it was mechanically sieved in the particle size range 900–1,200 μm, washed with distilled water and oven-dried at 120°C. A complete list of its chemical and physical properties is reported in Balsamo et al. [21].

Adsorption tests were carried out in batch mode using an organic-free mineral water whose chemical properties are representative of groundwater (pH = 8 and salinity = 0.46 mM); a complete list of its chemical properties are reported in Erto et al. [22]. The working solutions were prepared by spiking water samples with benzene/toluene stock solution (Sigma-Aldrich, Saint Louis, USA, 99.0%). The initial benzene/toluene concentrations used in each run were selected to keep equilibrium concentrations within the typical range for contaminated water. A variable amount of AC (0.3–1.5 g) was added to 100 mL headspace-free glass vessels of mineral water. For single-compound tests, the temperature was varied in the range 10°C–50°C, while the binary test was made at 20°C. In particular, the binary test was made on samples with the same volume, variable AC dosage (both as for single-compound tests) and same initial concentration ratio of the two analytes (i.e., $C^0_{ben}:C^0_{tol} = 1:1$, on molar basis), but different benzene and toluene initial concentrations for each experimental run. Benzene/toluene concentrations were measured with a gas chromatograph (Agilent, Santa Clara, USA, GC 6980) equipped with a flame ionization detector. A purge and trap system (Tekmar LSC-2000) was adopted for sample stripping from liquid phase.

To assure the accuracy, reliability and reproducibility of the collected data, all the adsorption tests were performed in triplicate and average values only were reported. The accuracy of the analytical technique was checked by the evaluation of the relative standard deviation (RSD) of each sample analysis. Typical values of the RSD for benzene/toluene analysis were below 5%.

3. Results and discussion

Adsorption tests on single-compound systems were carried out at four different temperatures, in order to determine the trend of isosteric heat of adsorption (ΔH) as a function of surface loading.

Fig. 1 reports the adsorption isotherms of benzene and toluene on F400 AC.

For both the compounds, the experimental results show that adsorption capacity decreases by increasing temperature, as expected due to the exothermicity of adsorption phenomena. For each temperature level, toluene is more adsorbed than benzene.

The experimental data of single compounds at different temperatures allowed calculating the heat of adsorption at constant amounts of adsorbate adsorbed, known as the isosteric heat of adsorption (ΔH, J/mol). This parameter can provide useful indications on the interactions between adsorbate and adsorbent, which, in turn, can be related to the different molecular structure of the adsorbates. The isosteric heat of adsorption corresponds to the ratio of the infinitesimal change in the adsorbate enthalpy and the infinitesimal change in the amount adsorbed. It can be calculated from the known Van't Hoff equation [22,23]:

$$\frac{d\ln(C)}{dT} = -\frac{\Delta H}{RT^2} \quad \text{or} \quad \frac{d\ln(C)}{d(1/T)} = \frac{\Delta H}{R} \qquad (1)$$

To this aim, the benzene/toluene equilibrium concentrations (C) at constant amount of adsorbed compound (ω) were taken from the experimental adsorption isotherm data at different temperatures (from Figs. 1(A) and (B)), and reported in Fig. 2.

The isosteric heat of adsorption (ΔH) at different amount of adsorbed benzene/toluene can be calculated as the slope of the plot of $\ln(C)$ vs. $(1/T)$ (Eq. (1)). The ΔH values are shown in Fig. 3.

In the range of surface coverage investigated, the thermodynamic analysis shows that the isosteric heat of adsorption of benzene is almost constant, also taking into account the error propagation of the analytical determination of benzene equilibrium concentration. This result implies both the energetic homogeneity of adsorption sites for benzene molecule and the absence of lateral interactions between benzene molecules adsorbed on carbon surface [23]. This is likely due to benzene molecule structure, perfectly symmetric and non-polar. On contrary, toluene isosteric heat of adsorption decreases by increasing the surface loading, remaining greater than the correspondent value of benzene, in particular for low AC surface coverage. In this case, the result is likely to be due to the interaction among the toluene molecules adsorbed rather than to a heteroenergetic character of adsorption sites [23]. In fact, the benzene and toluene adsorption mechanism is expected to be the same; hence, also the active sites involved on the carbon surface are expected to be the same. The only difference lies in the adsorbate molecule structures; indeed, the addition of a methyl group to the aromatic ring in the toluene molecule gives rise to a non-symmetric charge distribution, which can influence the interactions among adsorbed molecules. In general, it can be stated that the adsorption mechanism of aromatic molecules, such as benzene and toluene, involves dispersion interactions (i.e., London-Van der Waals forces) between the delocalized π electrons of the condensed polyaromatic carbon sheets

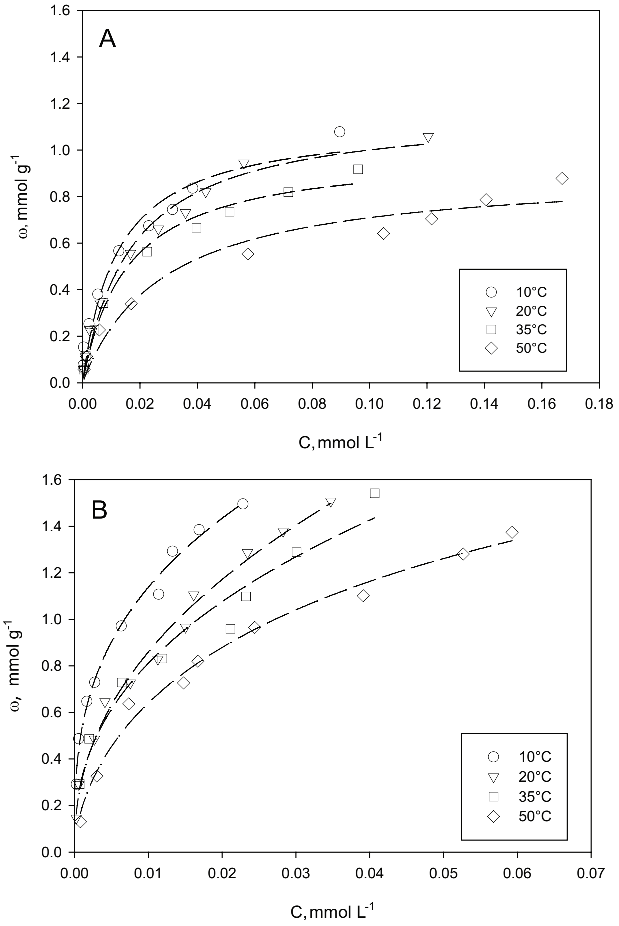

Fig. 1. Adsorption isotherms of benzene (A) and toluene (B) onto F400 as a function of temperature. Equilibrium pH = 8. Comparison with Langmuir (benzene) and Freundlich (toluene) model (lines).

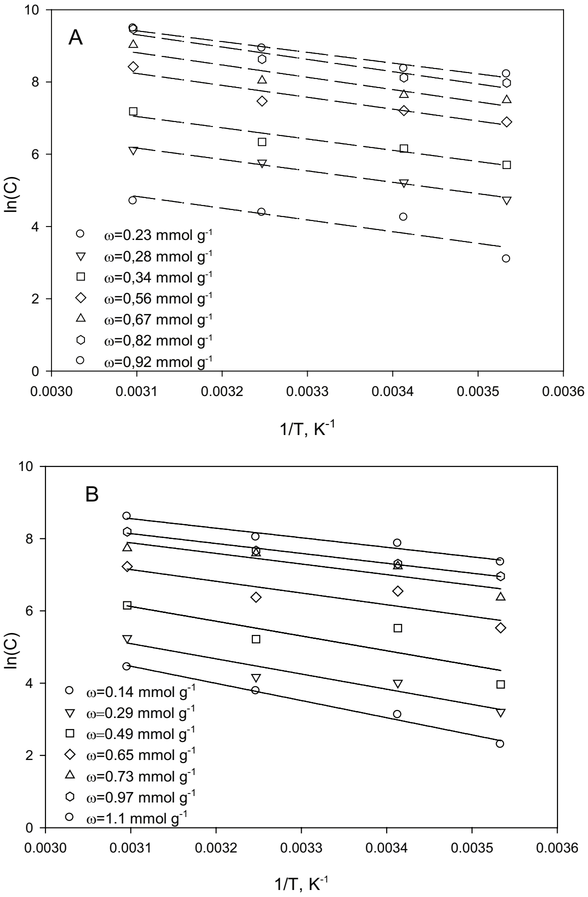

Fig. 2. Plots of ln(C) vs. 1/T at constant benzene (A) and toluene (B) adsorbed amount.

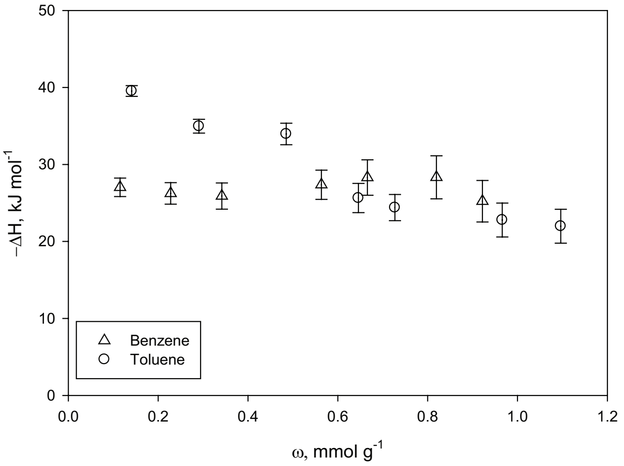

Fig. 3. Isosteric heat of adsorption (ΔH) of benzene and toluene on F400 activated carbon as a function of surface loading (ω).

and the aromatic molecule ring. The presence of an electron-donor functional group linked to the aromatic ring of toluene (i.e., methyl) determines an increase in the electronegativity of the ring and, consequently, stronger attractions with the nucleophilic carbon basal plane [14,20,24]. This can also explain the higher adsorption capacity of toluene, for each investigated temperature. It can be concluded that the different molecule configuration and polarity is likely to determine the different energetic interactions with carbon surface, then influencing also their overall adsorption capacities.

The determination of the best descriptive model for benzene/toluene adsorption onto AC is directly coupled with the individuation of the adsorption mechanism. In fact, each adsorption model assumes that the adsorption occurs by different mechanisms: monolayer isoenergetic adsorption (Langmuir), multienergetic adsorption sites (Temkin, Freundlich, Langmuir–Freundlich) and the micropore filling mechanism (Dubinin–Astakhov and Dubinin–Radushkevich) [22,23]. Organic compound adsorption is thought to be based on a micropore filling mechanism [23,25], but in dilute systems like those under analysis adsorption can also be described hypothesizing different mechanisms [22].

In order to test the classic adsorption model, a non-linear least-squares regression analysis on benzene and toluene adsorption experimental data was performed. The least residual sum of squares was used as a criterion for the best fitting parameter determination of each model.

The isotherm model equations and the model parameters for benzene and toluene adsorption at T = 20°C, taken as example, are reported in Tables 1 and 2, respectively. The analysis included the mean value and standard error of the parameters as well as the coefficient of determination (R^2).

From benzene adsorption data analysis, it can be observed that the best fitting models are Langmuir and Dubinin–Astakhov. However, the fundamental hypotheses of these models are markedly different, i.e., monolayer adsorption on isoenergetic sites and pore filling mechanism in multilayer on heteroenergetic sites, respectively. Based on the isosteric heat of adsorption analysis it was concluded that benzene adsorption on AC is isoenergetic under the experimental conditions investigated. Hence, even if multilayer adsorption cannot be definitely dismissed when dealing with the adsorption of an organic compound, it can be inferred that, in dilute solutions, benzene adsorption is likely to occur by a monolayer mechanism adequately described by the Langmuir model.

For toluene adsorption data, the best fitting models are Freundlich, Langmuir–Freundlich and Dubinin–Astakhov, while Langmuir model is far less performant. Also in this case, the results are consistent with the outcomes derived from isosteric heat of adsorption analysis, which highlighted the presence of heteroenergetic interactions between toluene molecules and AC surface, incompatible with the basic mechanism of Langmuir model. Hence, for toluene data modelling, the Freundlich model can be successfully used, also considering that the other models selected show a very high uncertainty in parameter estimation, as testified by their high relative standard errors.

For a deeper analysis of benzene/toluene adsorption mechanism, a binary test was carried out, also to test the occurrence of competition phenomena during their simultaneous adsorption on the same AC. As discussed above, benzene and toluene are expected to adsorb according the same mechanism, but adsorption phenomena strictly depend on analyte concentrations and molecule properties, hence, the behaviour of the binary system cannot be easily predicted.

Fig. 4 reports the experimental results of benzene and toluene binary adsorption. For both the analytes, the corresponding single-compound adsorption isotherm at the same temperature was also included, to allow for a direct comparison.

The analysis of the binary experimental data showed that toluene is adsorbed more largely than benzene, following

Table 1
Isotherm model parameters from benzene adsorption regression analysis at T = 20°C

Isotherm	Equation	Parameter	Value			R^2
			Mean	Standard error	t-Test	
Temkin	$\omega = B \cdot \ln(KC)$	K (L/mmol)	1.89×10^3	4.86×10^2	3.89	0.959
		B (mol/kg)	23.46	2.299	13.69	
Freundlich	$\omega = k \cdot C^n$	K (mol/kg)/(mmol/L)^n	2.62	2.65×10^{-1}	9.87	0.973
		n	0.680	3.87×10^{-1}	12.25	
Langmuir	$\omega = \frac{\omega_{\max} K \cdot C}{1 + K \cdot C}$	$\omega_{\max}$ (mol/kg)	1.17	7.05×10^{-2}	16.65	0.994
		ΔG (kJ/mol)	–9.88	3.2×10^{-1}	22.82	
		K (L/mmol)	5.77×10^1	1.09×10^1	5.31	
Langmuir–Freundlich	$\omega = \frac{\omega_{\max} (K \cdot C)^n}{1 + (K \cdot C)^n}$	$\omega_{\max}$ (mol/kg)	1.60	2.12×10^{-1}	7.55	0.979
		K (L/mmol)	8.54	4.14	2.06	
		n	6.73×10^{-1}	6.79×10^{-2}	9.90	
Dubinin–Radushkevich	$\omega = \omega_{\max} \exp\left[-\left(\frac{RT}{E} \ln\left(\frac{c_s}{c}\right)\right)^2\right]$	$\omega_{\max}$ (mol/kg)	2.41	0.71	3.41	0.990
		E (kJ/mol)	1.45×10^1	2.14	6.77	
Dubinin–Astakhov	$\omega = \omega_{\max} \exp\left[-\left(\frac{RT}{E} \ln\left(\frac{c_s}{c}\right)\right)^n\right]$	$\omega_{\max}$ (mol/kg)	1.75	2.63×10^{-1}	6.66	0.994
		E (kJ/mol)	1.68×10^1	1.05	16.03	
		n	2.65	0.39	6.73	

Table 2
Isotherm model parameters from toluene adsorption regression analysis at T = 20°C

Isotherm	Equation	Parameter	Value			R^2
			Mean	Standard error	t-test	
Temkin	$\omega = B \cdot \ln(KC)$	K (L/mmol)	3.97×10^{1}	1.58×10^{1}	2.52	0.901
		B (mol/kg)	2.61×10^{-1}	2.91×10^{-2}	9.03	
Freundlich	$\omega = k \cdot C^{n}$	K (mol/kg)/(mmol/L)^n	6.72	5.98×10^{-2}	11.25	0.989
		n	4.47×10^{-1}	2.20×10^{-2}	20.35	
Langmuir	$\omega = \frac{\omega_{\max} K \cdot C}{1 + K \cdot C}$	$\omega_{\max}$ (mol/kg)	1.83	1.94×10^{-1}	9.43	0.941
		ΔG (kJ/mol)	-1.12×10^{1}	2.4	18.52	
		K (L/mmol)	9.80×10^{1}	2,972	3.58	
Langmuir–Freundlich	$\omega = \frac{\omega_{\max} (K \cdot C)^{n}}{1 + (K \cdot C)^{n}}$	$\omega_{\max}$ (mol/kg)	1.92×10^{2}	8.21×10^{3}	0.23	0.989
		K (L/mmol)	3.54×10^{-2}	1.53	0.23	
		n	4.49×10^{-1}	2.74×10^{1}	4.88	
Dubinin–Radushkevich	$\omega = \omega_{\max} \exp\left[-\left(\frac{RT}{E} \ln\left(\frac{c_s}{c} \right) \right)^{2} \right]$	$\omega_{\max}$ (mol/kg)	3.57	1.84	1.94	0.978
		E (kJ/mol)	1.31×10^{4}	3.33×10^{3}	3.93	
Dubinin–Astakhov	$\omega = \omega_{\max} \exp\left[-\left(\frac{RT}{E} \ln\left(\frac{c_s}{c} \right) \right)^{n} \right]$	$\omega_{\max}$ (mol/kg)	1.41×10^{2}	5.86×10^{2}	0.24	0.991
		E (kJ/mol)	8.17×10^{2}	3.16×10^{3}	0.26	
		n	5.55×10^{-1}	4.53×10^{-1}	1.23	

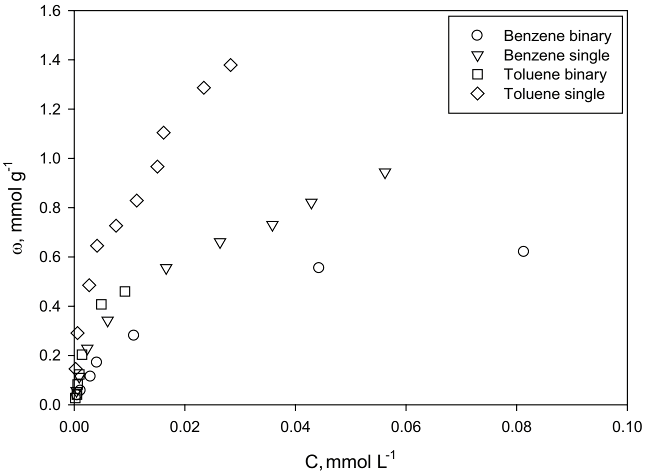

Fig. 4. Benzene and toluene adsorption isotherms in binary system (1:1, on molar basis) onto F400 activated carbon. T = 20°C, equilibrium pH = 8. Comparison with single-compound data.

the same behaviour of the corresponding single-compound systems. This result is consistent with those reported in previous works dealing with the adsorption of organic compounds from water [26]. Moreover, a significant reduction in adsorption capacity – with respect to the corresponding single-compound data – was observed for both the compounds (except for a very low concentration range, in which single-compound and binary adsorption data almost overlap), indicating a competitive adsorption towards the same active sites.

The interference and competition phenomena arising in such systems can be described and, in some cases, predicted by specific adsorption models whose mathematical formulation can be more or less complex, depending on the physical adsorption mechanism hypothesized. Preliminarily, it can be observed that, in the Henry region, the low coverage and the consequent absence of any relevant interaction makes the use of complex multicomponent models unnecessary, as the single-compound counterparts generally provide good results. For the system under investigation, this evidence was verified only in a short concentration range, so that a dedicated binary adsorption analysis was mandatory. To this aim, a multicomponent Langmuir model was initially chosen for its simplicity and low number of fitting parameters, easily valuable through single-compound experimental tests [26]. The equations representing the multicomponent Langmuir adsorption model are reported in some major works on adsorption [23]. The equation representing the adsorption model tested for binary adsorption analysis is reported in the following, while the description of the main assumption and basic hypotheses behind its formulation is described in fundamental literature on adsorption [23].

$$\omega_1 = \omega_{1,\max} \frac{K_1 C_1}{1 + K_1 C_1 + K_2 C_2} \tag{2}$$

where ω_1 is compound 1 adsorption capacity, $\omega_{1,\,\mathrm{MAX}}$ is the correspondent maximum value and C_i and K_i (i = 1, 2) are equilibrium concentration and adsorption constant, respectively.

The comparison between Langmuir multicomponent model and binary experimental data (not reported) provided average results until a definite AC surface coverage (approximately equal to 0.2 mmol/g). For higher values, the model proved to be substantially inadequate for both compounds.

Indeed, the application of Langmuir multicomponent model requires the acceptance of its basic assumptions, first the presence of active sites with identical energy and the absence of interactions between the molecules adsorbed [27]. These hypotheses appear to be too much restrictive for certain systems in particular when heterogeneous solids such ACs are used.

In order to find a valid model in the entire range of equilibrium concentration tested, the binary experimental data were analyzed in light of the IAST model [28]. The IAST model provides a thermodynamically consistent method for predicting multicomponent adsorption isotherms, using single-compound isotherm data. The IAST model is based on the assumption that the adsorbed mixture forms an ideal solution in equilibrium with liquid phase at a constant spreading pressure for each solute (π_i), in analogy with Raoult's law for vapour–liquid equilibria. Moreover, it hypothesizes a reduction in adsorption capacity of both compounds in binary system with respect to the single-compound counterpart, and proportional to the latter. In the IAST model, the following five basic equations are used to predict multicomponent adsorption capacity from the corresponding single-compound data:

$$C_i = C_i^0(T,P,\pi)\cdot z_i \quad i = 1 \ldots N \tag{3}$$

$$z_i = \frac{\omega_i}{\omega_T} \quad i = 1 \ldots N \tag{4}$$

$$\omega_T = \sum_{i=1}^{N} \omega_i \tag{5}$$

$$\frac{1}{\omega_T} = \sum_i \frac{z_i}{\omega_i^0} \quad i = 1 \ldots N \tag{6}$$

$$\pi_i(C_i^0) = \frac{RT}{A}\cdot\int_0^{C_i^0} \frac{\omega_i^0(C_i^0)}{C_i^0}\,dC_i^0 \quad i = 1 \ldots N \tag{7}$$

where C_i is the equilibrium liquid concentration of adsorbates in multicomponent system; C_i^0 is the equilibrium liquid concentration of adsorbates in the single-compound system; ω_i^0 is the single-compound adsorption capacity calculated, at same pressure, temperature and spreading pressure of the multicomponent system; z_i is the mole fraction of each compound on carbon surface; ω_T is the total surface loading, i.e., the sum of solutes adsorption capacities (ω_i) in the multicomponent system; A is the specific adsorbent area; R is the universal gas constant and T is the absolute temperature.

Further details on the IAST model are reported in Erto et al. [26]. The application of the model requires an appropriate single-compound adsorption model, so as to allow for a reliable prediction of multicomponent adsorption data. In this work, the Langmuir equation parameters obtained from the single-compound systems (Tables 1 and 2) were used as they provide the best comparative results. In Fig. 5, the results of the IAST modelling analysis are reported.

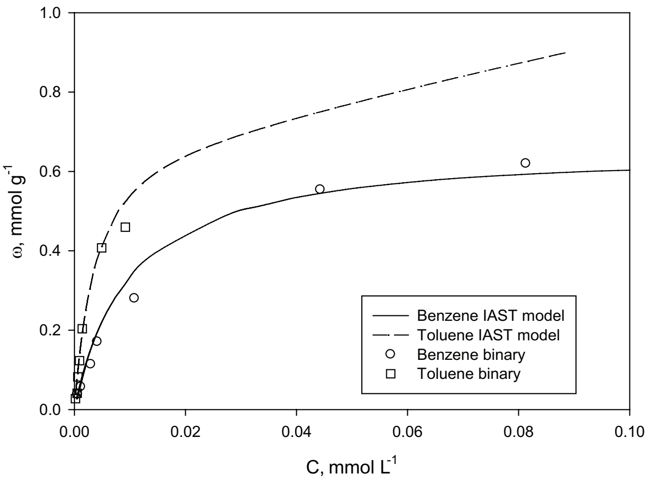

Fig. 5. Modelling of benzene/toluene binary adsorption system (C^0_{ben}:C^0_{tol} = 1:1) by IAST model.

It can be observed that the modelling results are very satisfying for both compounds, as the adsorption capacity is correctly predicted on the entire range of equilibrium liquid concentration tested, as requested. It can be deduced that the binary system tested has an ideal behaviour under the experimental conditions used; hence, the interactions between the adsorbed molecules can be considered as negligible. This result is in line with the adsorption mechanism derived from the thermodynamic analysis reported above. In fact, even if for toluene the presence of lateral interactions can be reasonably expected also in binary system, their occurrence can be neglected because of the lower equilibrium concentrations tested, which in turn are due to its significantly higher adsorption capacity (Fig. 4). In conclusion, the IAST model is a valid tool for the prediction of adsorption data of the investigated system and the predictable character of the model allows it to be applied to wider experimental data, until lateral interactions between adsorbed molecules arise and determine a non-ideal behaviour of the system.

4. Conclusions

The adsorption of benzene and toluene from simulated ground water onto AC, both in single-compound and binary systems, was studied. Experimental results in single-compound systems showed that, for each temperature, toluene is adsorbed more than benzene.

The analysis of isosteric heat of adsorption shows that lateral interactions occur among the toluene molecules adsorbed, which are likely due to the addition of an electron-donor functional group (i.e., methyl) to the aromatic ring of the molecule. This group gives rise to a non-symmetric charge distribution, an increase in the electronegativity of the ring and stronger attractions with the nucleophilic carbon basal plane, thus influencing also the overall adsorption capacity.

The experimental data on binary system show that toluene is more adsorbed than benzene, mirroring the same behaviour of the corresponding single-compound systems. However, a significant reduction in adsorption capacity, with respect to the correspondent single-compound data, was observed for both the compounds, indicating the occurrence of competitive adsorption towards the same active sites. The Langmuir multicomponent model, often proposed for the interpretation of binary adsorption data, provides poor results while a very good data prediction can be obtained by the IAST model in the entire range of the equilibrium concentrations tested.

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