CHEMICAL ENGINEERING TRANSACTIONS

VOL. 32, 2013

Chief Editors: Sauro Pierucci, Jiří J. Klemeš
Copyright © 2013, AIDIC Servizi S.r.l.,
ISBN 978-88-95608-23-5; **ISSN** 1974-9791

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at: www.aidic.it/cet

DOI: 10.3303/CET1332012

Single and Competitive Adsorption of Toluene and Naphthalene onto Activated Carbon

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In this work, an experimental and modelling analysis of Toluene/Naphthalene adsorption from water solution on a commercial activated carbon both in single and binary systems was carried out. All the experimental tests were conducted at constant pH=7 and temperature (20 °C). Experimental results indicate that Toluene has the highest adsorption capacity in single compound systems and competitive effects arise when the two analytes are adsorbed simultaneously.

1. Introduction

The contamination of surface water and groundwater by aromatic compounds is one of the most serious environmental problems (Iovino et al., 2008); it is estimated that several coastal areas and water bodies in the industrialized countries have contaminated sediments that can release many hazardous compounds for human health and environment.

Polycyclic Aromatic Hydrocarbons (PAHs) are ubiquitous contaminants resulting from the burning of fossil fuels (and, more generally, organic material), and they are present in the environment as a mixture of many compounds (Ania et al., 2011). In water or in the environment PAHs go through a very slow biodegradation because of the aerobic conditions and they are generally resistant to hydrolysis processes. PAHs with low number of aromatic rings are the most soluble in water and can cause persistent contamination of the environment.

Due to their acute toxicity and potentially carcinogenicity, aromatic compounds are considered as hazardous as well and they are submitted to a strict regulation (IARC, 2002). Therefore, the removal of all these compounds from polluted water is becoming one of the most important environmental concerns (Capasso et al., 2007).

Remediation technologies for contaminated water mainly include air stripping, often coupled with thermal treatments, advanced oxidation processes (Fenton, (ozone, hydrogen peroxide, etc.) or adsorption mainly by activated carbons. In particular, groundwater treatments can be ex-situ by pump and treat technique or performed in-situ with Permeable Reactive Barriers (Erto et al., 2011a).

Activated carbon adsorption is widely used to remove pollutants from water and wastewater due to its good removal efficiencies and to its great versatility. It is commonly adopted for the removal and recovery of aromatic compounds in water and sewage due to its high surface area, tunable porosity and general chemical affinity with such compounds (Zhang et al., 2006).

The design of adsorber units mainly depends on the equilibrium adsorption capacity of the sorbent in the working conditions (Leone et al., 2012). At the moment, these data are available in a limited number of experimental conditions and, as to activated carbons, there are no predictive models to assess their adsorption capacity as a function of the process parameters (Erto et al., 2012). This makes adsorber design a complex and approximated task. Moreover, natural and industrial polluted water streams usually contain a mixture of several pollutants (Salvestrini et al., 2010).

Please cite this article as: Iovino P., Canzano S., Capasso S., Di Natale M., Erto A., Lama A., Musmarra D., 2013, Single and competitive adsorption of toluene and naphthalene onto activated carbon, Chemical Engineering Transactions, 32, 67-72 DOI: 10.3303/CET1332012

The analysis and modelling of experimental data involving such systems present intrinsic difficulties due to the great variety of experimental conditions (mainly in terms of pollutant concentrations) that can determine the occurrence of an unpredictable competition for the same adsorption sites of the solid surface, interactions between adsorbed molecules and, consequently, a great variation in the adsorption capacities of the analytes (Erto et al., 2011b).

In particular, the competitive and/or cooperative mechanism of adsorption of aromatic compounds is not yet clear (Zhang et al., 2006).

The object of this work is an experimental and modelling analysis of Toluene (TOL) and Naphthalene (NAP) adsorption both in mono- and binary systems on a commercial granular activated carbon (Filtrasorb 400).

Batch tests were conducted at constant pH (7) and temperature (20 °C). In particular, binary tests were carried out with different initial concentration ratios of the two analytes ($C^0_{TOL}:C^0_{NAP}$), to extend the field of equilibrium mixture composition.

2. Materials and methods

2.1 Adsorbent

A commercial activated carbon produced starting from bituminous coal, Filtrasorb 400 (F400), purchased from Calgon Carbon Corporation, was used for all the experimental runs. The raw material was gently crashed and sieved in order to obtained grains in the range 1.0–2.0 mm.

Before the adsorption experiments, the sieved material was repeatedly washed with deionized water (50 mL water for 1 g activated carbon) until the rinse water showed no change in the conductivity after 1 day of contact. Finally the samples were dried at 40 °C. Adsorbent properties are reported in Erto et al. (2010).

2.2 Adsorbates

The Toluene and Naphthalene employed were of analytical grade with purity higher than 99 % and purchased from Sigma-Aldrich (Saint Louis, USA). These chemicals were diluted using deionized water to the desired concentrations.

2.3 Batch adsorption tests

Adsorption working solutions were prepared by spiking water samples with Toluene and/or Naphthalene stock solutions, both for mono and binary tests. A variable amount of activated carbon, 1.0-50 mg, was added to a 50 mL amber glass bottle. The initial Toluene/Naphthalene concentrations used in each run were selected so that the equilibrium concentrations were in the typical range for contaminated water (initial concentration range: 0.055 - 0.11 mmol L-1). Batch tests were conducted at constant pH (7) and the samples were stored for a week at 20 °C and daily shacked. Afterward, the liquid phases were analyzed by gas chromatography/mass spectrometry (GC/MS).

2.4 Gas chromatographic analyses

Prior to chromatographic analyses, 1.0 mL of hexane was added to the solution and the mixture was vigorously shacked for 10 min, then the mixture was allowed to settle and 1.0 mL of the hexane solution was taken by a suitable syringe and injected in a gas chromatograph. The analysis was then performed with Agilent Technologies 7890A/5975C GC/MS, equipped with a HP-5MS column (length: 30 m, internal diameter: 0.25 mm, film thickness: 0.25 µm.

The concentration of Toluene and Naphthalene was calculated by the standard solution calibration method based on a six-point calibration curve. The relative standard deviation of this experimental procedure was about 6 %.

3. Results and Discussion

The adsorption isotherms of Toluene and Naphthalene at T=20 °C, in single-compound systems, on F400 are reported in Figure 1. For both the compounds, the adsorption capacity increases with equilibrium concentration but an asymptotic value is not reached in the investigated range of equilibrium concentrations. The adsorption capacity values are in agreement with those found by other authors (Monneyron et al., 2003) for the adsorption of the same compounds on activated carbon. .

The experimental results also indicate that Toluene is adsorbed to a greater extent than Naphthalene, probably due to a different steric hindrance of the molecules. A complete sorbent characterization, in fact, showed that Filtrasorb 400 is a microporous solid with a narrow pore size distribution (Morlay and Joly, 2010).

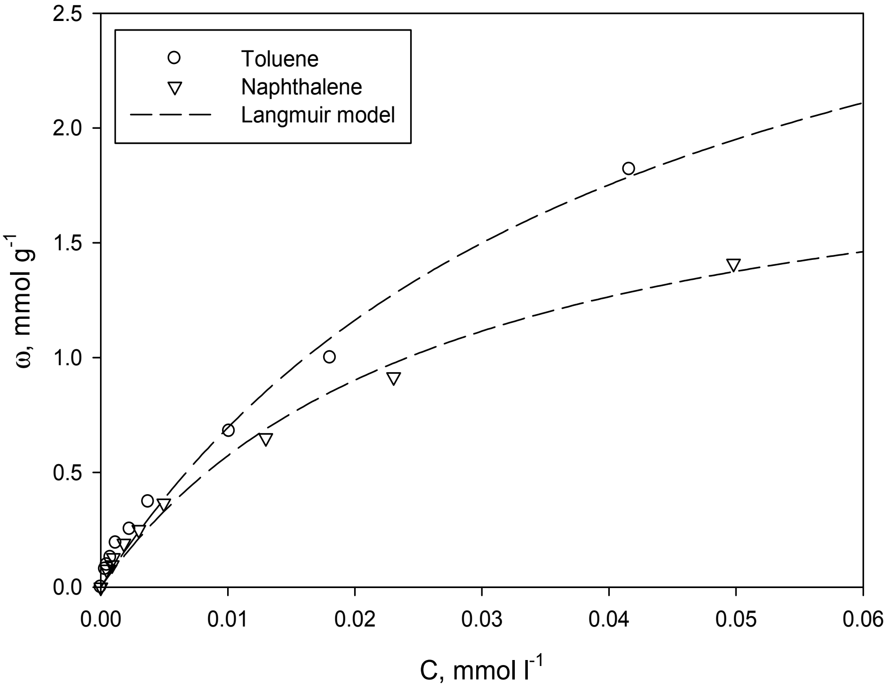

Figure 1 Adsorption isotherms of Toluene and Naphthalene onto Filtrasorb 400 GAC. T=20 °C, pH=7. Comparison between experimental data (symbols) and Langmuir model results (lines)

The most frequently adopted adsorption models were used to analyse experimental data and Langmuir and Freundlich resulted to be the most suitable. In Table 1, the model parameters, as derived from a non-linear regression analysis, are reported together with the correspondent standard error and the determination coefficient (R^2). As can be observed, for both compounds the two models showed a high R^2 with a slight predominance of Langmuir model. In Figure 1, the fitting of experimental data with Langmuir model is reported, confirming its suitability for the description of adsorption isotherms of both analyses.

Table 1: Langmuir and Freundlich model parameters and determination coefficient (R^2) for Toluene and Naphthalene adsorption regression analysis

Isotherm	**Equation**	**Parameter**	**Value**		**R^2**
			Mean	**Std error**	
Toluene:					
Freundlich:		K (mmol/g)/(mmol/l)^n	15.48	0.59	0.989
		n	0.67	0.01	
Langmuir:	$\omega=\frac{\omega_{\max}K\cdot C}{1+K\cdot C}$	ω_{max} (mmol/g)	3.56	0.51	0.987
		K (l/mmol)	24.26	5.81	
Naphtalene:					
Freundlich:	$\omega=k\cdot C^n$	K (mmol/g)/(mmol/l)^n	8.65	0.33	0.988
		n	0.60	0.010	
Langmuir:	$\omega=\frac{\omega_{\max}K\cdot C}{1+K\cdot C}$	ω_{max} (mmol/g)	2.12	0.17	0.990
		K (l/mmol)	37.05	6.12	

The experimental tests on binary systems were carried out with nine samples, all having the same volume, activated carbon dosage and initial concentration ratio of the two analytes (C^0_{TOL} :C^0_{NAP}), but each experimental point corresponding to different Toluene and Naphthalene initial concentrations in order to describe two complete adsorption isotherms in the concentration range of typical polluted waters. Three adsorption binary test series were performed, corresponding to different initial concentration ratios of the two analytes: C^0_{TOL} :C^0_{NAP}=1:1; C^0_{TOL} :C^0_{NAP}=1:1.4; C^0_{TOL} :C^0_{NAP}=1.4:1. The experimental results for each adsorption run are reported in Figure 2.

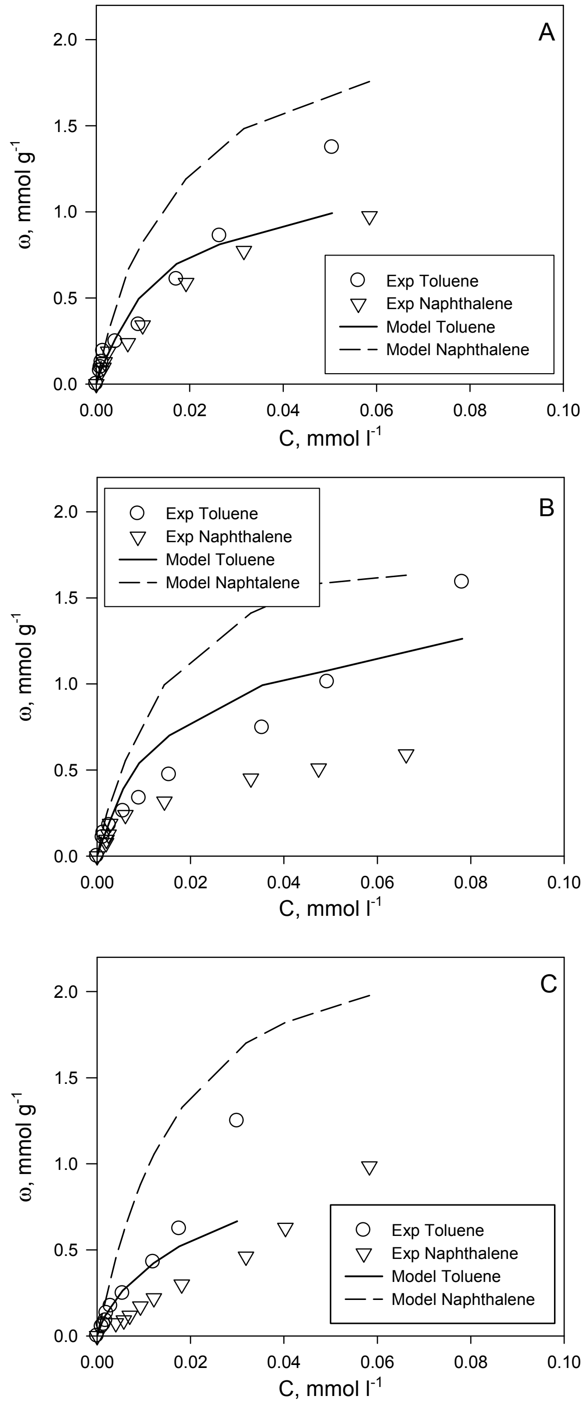

Figure 2: Adsorption tests in Toluene/Naphthalene binary systems for different initial concentrations ratio: A) C^0_{TOL} :C^0_{NAP}=1:1; B) C^0_{TOL} :C^0_{NAP}=1:1.4 ; C) C^0_{TOL} :C^0_{NAP}=1.4:1. T=20°C, pH=7.

The experimental tests allowed the determination of multicomponent adsorption isotherms. The experimental data show that, for each binary adsorption run, Toluene adsorption capacity is higher than that of Naphthalene. A change in the initial concentration ratio determines a marked effect on Naphthalene adsorption capacity and a lower effect on Toluene adsorption. However, for both compounds, the adsorption capacity in binary systems is lower than in single-compound systems, which is likely to be due to a competition for the same active sites.

In order to provide a deeper analysis of the entire set of experimental data, all the binary adsorption isotherms were analyzed by Langmuir multicomponent model, whose expression is reported in the Equation (1):

$$\omega_1 = \omega_{1,MAX} \frac{K_1 C_1}{1 + K_1 C_1 + K_2 C_2} \qquad (1)$$

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

The application of Langmuir multicomponent model requires the acceptance of its basic assumptions valid for single-compound adsorption: (i) a homogeneous sorbent surface in terms of energy of adsorption, (ii) no interaction between adsorbed species, (iii) all adsorption sites are equally available to all adsorbed species.

It is here recalled that the adsorption constants of both compounds ($\omega_{i,MAX}$ and K_i) should be derived individually from single-compound adsorption tests, as they represent intrinsic properties of the sorbate-adsorbent couple. Moreover, in the Equation (1) ω_{1MAX} is a constant value for both compounds as it is an intrinsic property of the adsorbent.

A rigorous application of Langmuir multicomponent model to the experimental data set seemed non-adequate, except for very low concentration values for which the competitive effect appeared to be weak. The regression analysis reported in Figure 2 showed a significant deviation between model predictions and experimental values, in particular for Naphthalene. Indeed, the model provides an acceptable prediction of Toluene adsorption data but it greatly overestimates the Naphthalene adsorption capacity. The basic hypotheses of this model, in fact, resulted to be too much restrictive for these systems in particular when heterogeneous solids such as activated carbon are used; moreover, in previously published works (Erto et al., 2009) the occurrence of lateral interactions among organic molecules were founded. These interactions are likely to be due to their asymmetrical shape (as for Toluene) and can affect the general application of the Langmuir multicomponent model.

4. Conclusions

In this work, Toluene and Naphthalene adsorption tests both in mono- and binary systems were carried out at constant pH (7) and temperature (20 °C). In particular, binary tests have been carried out with different initial concentration ratios of the two analytes (C^0_{TOL} :C^0_{NAP}), to extend the fie ld of equilibrium mixture composition.

Experimental results indicated that Toluene is adsorbed to a greater extent than Naphthalene, both in single and binary systems, presumably because of a different steric hindrance of the molecules. Moreover, for both compounds, the adsorption capacity in binary systems resulted to be lower than in single-compound systems, probably due to a competition for the same active sites.

Finally a modeling analysis showed that the Langmuir model can adequately fit the set of single-compounds experimental data, while for the binary systems it is adequate only in a very low range of concentration values. For higher concentrations, the model provides an acceptable prediction of Toluene adsorption data but it greatly overestimates the Naphthalene adsorption capacity.

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