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Experimental and isotherm-models analysis on TCE and PCE adsorption onto activated carbon

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This work presents an isotherm-models analysis on adsorption of trichloroethylene (TCE) and tetrachloroethylene (PCE) from aqueous solution on activated carbon. Starting from experimental tests, the analysis of adsorption mechanisms is carried out through the evaluation of the isosteric heat of adsorption of both compounds. It shows the presence of lateral interactions between TCE molecules adsorbed on carbon surface, absent for PCE's. Furthermore, a modelling analysis is performed and a statistical method for the individuation of the best data fitting model, among the commonly adopted, is suggested.

1. Introduction

Chlorinated ethenes such as tetrachloroethylene (PCE) and trichloroethylene (TCE) are among the most widely occurring and toxic organic groundwater contaminants, due to their widespread use (EPA, 1992). The removal of these compounds from polluted groundwater is a necessary task and adsorption on activated carbon represents a commonly adopted technology. Despite the large industrial application of this technology, the mechanisms of adsorption on carbon surface has received limited attention, while extensive researches have been focused in the past decades on the adsorption phenomenology.

In summary, the experimental studies have been mainly focused on how the activated carbon properties influence their adsorption capacity towards TCE and PCE (Li *et al.*, 2002; Bembnowska *et al.* 2003; Quinlivan *et al.*, 2005). The analysis of the influence of the solution properties on TCE adsorption has been also addressed on the competition effects of humic substances, such as Natural Organic Matter (NOM) (Quinlivan *et al.*, 2005). Finally, Li *et al.* (2002) have found that activated carbons with a low oxygen and nitrogen content are the most effective for TCE removal from aqueous solutions.

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A deep comprehension of the mechanisms and the role of process parameters is the first mandatory step for any attempt to a process optimization. In this sense, this work aims to analyse the dynamics of TCE and PCE adsorption from laboratory-reproduced groundwater on activated carbon. Adsorption isotherms of TCE/PCE solutions at neutral pH and different temperature levels have been experimentally determined. The analysis of experimental data has been addressed to the determination of the isosteric heat of adsorption for the individuation of the adsorption mechanism and for the determination of the factors affecting the magnitude of TCE and PCE adsorption capacity. A modelling analysis has been performed for the description of experimental results and, finally, a statistical method to identify the best data fitting model, among those commonly adopted, has been suggested.

2. Materials and methods

2.1 Sorbents characteristics

Aquacarb 207EA^{TM} is a commercially available non impregnated granular activated carbon, deriving from a bituminous coal. This material has a BET surface area of 950 m^2/g and an average pore diameter around 26 Å. Sorbent particles with averaged diameter between 1 and 1.2 mm has been used in this work.

The sorbent is slightly alkaline ($pH_{PZC} = 8$) and its surface functional groups, obtained with the Boehm's titration analysis, are mainly represented by basic active sites.

A complete list of chemical properties of the sorbent is reported in Erto (2007).

2.2 Experimentals

In all experimental runs, the samples for the adsorption tests were prepared by adding the analytes TCE (99,5%, Sigma Aldrich) or 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). A complete list of properties is reported in Erto (2007).

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 aluminium sheet to prevent photodegradation phenomena. Preliminary tests show that a contact time of 72 hours is required to reach equilibrium conditions. At equilibrium, both the analyte concentrations in solution and on the carbon surface have been measured.

The analyte solution concentrations were measured with a gas chromatograph (Agilent, GC 6980) equipped with a capillary column (DB-624, 30 m x 0.32 mm x 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.

A maximum error of 7% in the analyte material balance is allowed as accuracy index.

3. Results and discussion

3.1 Experimental results

In order to investigate the isosteric heat of adsorption (ΔH) trend with surface loading and the effect of temperature, adsorption isotherms of TCE and PCE on Aquacarb 207EA^{TM} have been reported in Figure 1 for different temperature levels. For both the analytes, the adsorption capacity decreases with temperature, in agreement with the exothermicity of adsorption phenomena. Moreover, for each temperature, the TCE adsorption capacity is lower than PCE's.

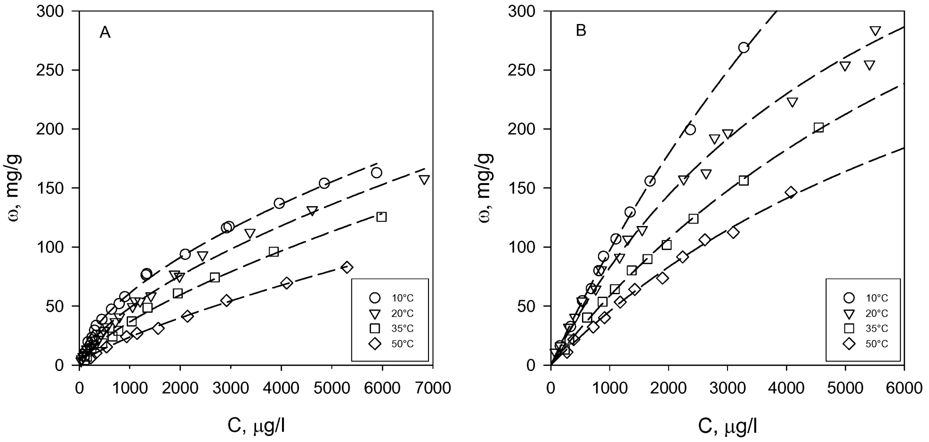

Figure 1 - Adsorption isotherms of TCE (A) and PCE (B) onto Aquacarb 207EA™ as a function of temperature. Equilibrium pH=7.

3.2 Thermodynamic analysis

The isosteric heat of adsorption (*ΔH*) for both analytes can be calculated from the following thermodynamic relationship derived from the Van't Hoff equation:

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

For this aim, the equilibrium concentrations (*C*) at constant amount of surface loading (ω) are taken from the adsorption isotherms data at different temperatures. Following this path, the *ΔH* is calculated from the slope of the plot of ln(*C*) versus (1/*T*) for different amount of each analyte adsorbed (see equation 1). The *ΔH* values are shown in Figure 2 as a function of the surface loading. For PCE, the isosteric heat of adsorption is constant with surface loading, indicating both the energetic homogeneity of adsorption sites towards PCE adsorption and the absence of lateral interactions between PCE molecules adsorbed on carbon surface (Suzuki, 1990). Differently, for TCE the isosteric heat of adsorption decreases by increasing the surface loading. This result can be related to the interaction among adsorbed molecules (Suzuki, 1990), since the TCE and PCE adsorption mechanism is expected to be the same. Indeed, for both the molecules, adsorption is likely to occur by dispersion interactions (i.e. London-Van Der Walls forces) between delocalized π-electrons of the polyaromatic carbon sheets and the highly oxidized TCE/PCE molecule double bond (EPA, 1992; Erto, 2007). The different polarity of TCE and PCE molecules (which is equal to zero for the latter) can play an important role in the interaction on carbon surface, then determining the different adsorption capacities of TCE and PCE. Moreover, the highest chlorine content in PCE molecule determines a higher oxidation and molecule stabilization that enhances the adsorption on carbon surface having nucleophilic character (EPA, 1992).

According to these results, the Freundlich and the Langmuir models are expected to have the higher physical meaning for TCE and PCE adsorption description respectively.

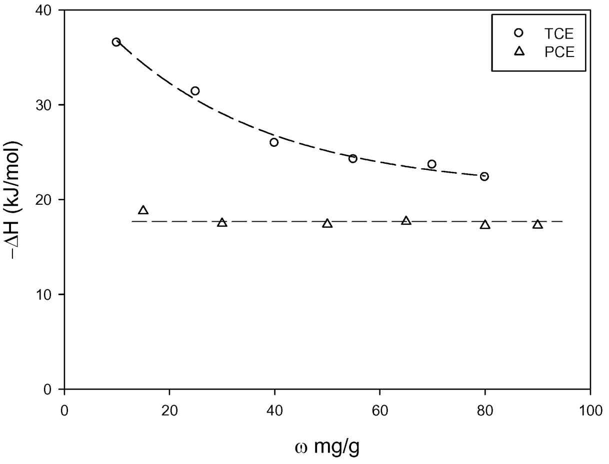

Figure 2 – Isosteric heat of adsorption (ΔH) as a function of surface loading (ω) for TCE and PCE adsorption on activated carbon

3.3 Adsorption isotherm models analysis

In this work, several models have been tested for the experimental data fitting, using nonlinear least-squares regression analysis. The least residual sum-of-squares (ResSS) has been used as a criterion for the best fitting parameters for each model. The isotherm equations and the model parameters from TCE adsorption regression analysis, at T=20°C taken as example (from Figure 1), have been reported in Table 1.

Since the coefficient of determination (R^2) is very high for each model, a more in-depth statistical analysis has been carried out through an ANOVA analysis on regression residuals of each model, commonly referred to as *lack-of-fit test* (Montgomery, 2001).

This method can be used whenever data points are replicated. It consists in a F-test as the ratio between two terms, each divided by appropriate degrees of freedom: the lack-of-fit sum of squares (LofSS) for fitting the averages of replica, which includes systematic as well as random errors, and pure-error components sum of squares (ErrSS), which reflects only random variations, because it is based on differences between replicated response values at the same point. The ratio follows an F-distribution; if the experimental F-value (as $F_{\upsilon_{lof},\upsilon_{err}}$ in table 2) is greater than an upper-tail cut-off from the F-distribution at a settled significance level, then the observed variation of dependant variable is not just random or due to experimental errors but it indicates that the functional part of the model is incomplete or inadequate to explain this variation (Montgomery, 2001).

In this paper, the significance levels have been set to 95% and 99%. Hence, if the experimental F-value exceeds the F-distribution cut-off value, there is only 5% and 1% of probability, respectively, that the model is adequate due to random fluctuations in the data. The cut-off values from published F-tables (named F(0.05) and F(0.01)) are reported in Table 2, as a function of LofSS and ErrSS degrees of freedom and together with the results of the lack-of-fit test.

Table 1 - Isotherm equations and model parameters from TCE and PCE adsorption regression analysis at T=20°C

Isotherm	**Equation**	**Parameter**	**Value**		**R^2**
			Mean	**Std error**	
TCE:					
Freundlich:	$\omega = k \cdot C^n$	K (mg/g)/(μg/l)^n n	0.436 0.680	0.037 0.011	0.9964
Langmuir:	$\omega = \frac{\omega_{\max} K \cdot C}{1 + K \cdot C}$	ω_{max} (mg/g) ΔG (kJ/mol) K (l/mol)	238.7 -25.39 33787	13.32 0.214 2972	0.9928
Dubinin-Radushkevich:	$\omega = \omega_{MAX} \exp\left[-\left(\frac{RT}{E} \ln\left(\frac{c_s}{c} \right) \right)^2 \right]$	ω_{max} (mg/g) E (kJ/mol)	594.7 10.68	22.86 0.101	0.9959
Dubinin-Astakhov:	$\omega = \omega_{MAX} \exp\left[-\left(\frac{RT}{E} \ln\left(\frac{c_s}{c} \right) \right)^n \right]$	ω_{max} (mg/g) E (kJ/mol) n	1450.1 7.112 1,419	590.0 1.408 0.186	0.9972
PCE:					
Freundlich:	$\omega = k \cdot C^n$	K (mg/g)/(μg/l)^n n	0.776 0.682	0.134 0.021	0.9921
Langmuir:	$\omega = \frac{\omega_{\max} K \cdot C}{1 + K \cdot C}$	ω_{max} (mg/g) ΔG (kJ/mol) K (l/mol)	567.4 -24.95 28190	35.44 0.254 2949	0.9927
Dubinin-Radushkevich:	$\omega = \omega_{MAX} \exp\left[-\left(\frac{RT}{E} \ln\left(\frac{c_s}{c} \right) \right)^2 \right]$	ω_{max} (mg/g) E (kJ/mol)	741.2 8.771	27.69 13.00	0.9936
Dubinin-Astakhov:	$\omega = \omega_{MAX} \exp\left[-\left(\frac{RT}{E} \ln\left(\frac{c_s}{c} \right) \right)^n \right]$	ω_{max} (mg/g) E (kJ/mol) n	1020.0 7.419 1.639	307.9 1235.0 0.275	0.9942

The results show that the only models adequate to describe the TCE experimental data are Freundlich and Dubinin-Astakov, even if the latter shows a bigger statistical uncertainty (cfr. Table 1). Furthermore, the lack-of-fit test clearly shows that the Langmuir model is inadequate at a 99% confidence level. For PCE, conversely, all the models are inadequate at a 95% confidence level (but not as up to a 99% confidence level), except the Langmuir. These results are consistent with the indication deriving from the isosteric heat of adsorption analysis, as reported in section 3.2. In fact, the Langmuir model hypothesizes both isoenergetic adsorption sites and no lateral interaction between adsorbed molecules, while the thermodynamic analysis has clearly stated that these properties can be verified simultaneously only for PCE adsorption.

4. Conclusions

In this work, an isotherm model analysis on adsorption of TCE and PCE on activated carbon from model water solutions has been carried out. Starting from experimental tests, the evaluation of the isosteric heat of adsorption has shown the presence of lateral interactions between TCE molecules adsorbed on carbon surface, absent for PCE's. The different polarity of TCE and PCE molecules seems to play an important role in the interactions with carbon surface, then influencing their adsorption capacity. A statistical analysis of experimental data has been performed through an ANOVA test (lack-of-fit test). This analysis has shown that, in accordance with the isosteric heat indications, the Freundlich and the Langmuir model are the best data fitting for TCE and PCE adsorption respectively.

Table 2 – Results of lack-of-fit test for adsorption models analysis

Model	**LofSS** (σ^2_{err})	**LofDF** (ν_{lof})	**ErrSS** (σ^2_{lof})	**ErrDF** (ν_{err})	$F_{\upsilon_{lof},\upsilon_{err}} = \frac{\sigma^2_{lof}/\upsilon_{lof}}{\sigma^2_{err}/\upsilon_{err}}$	**F(0.05);** **F(0.01)**
TCE:						
Freundlich:	596.7	23	566.7	35	1.60	1.84; 2.38
Langmuir:	1263.8	23	566.7	35	3.39	1.84; 2.38
Dubinin-Radushkevich:	715.5	23	566.7	35	1.92	1.84; 2.38
Dubinin-Astakhov:	626.8	22	566.7	35	1.76	1.85; 2.40
PCE:						
Freundlich:	1302.6	20	497.6	22	2.87	2.10; 2.90
Langmuir:	1210.1	20	497.6	22	1.82	2.10; 2.90
Dubinin-Radushkevich:	1063.5	20	497.6	22	2.35	2.10; 2.90
Dubinin-Astakhov:	966.8	19	497.6	22	2.25	2.13; 2.96

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