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Experimental and statistical analysis of trichloroethylene adsorption onto activated carbon

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ABSTRACT

Adsorption processes have long been used in water and wastewater treatment and a deterministic approach has been often adopted for the analysis of fundamental mechanisms.

In this research, a new approach based on statistical treatment of modelling data is adopted for the analysis of trichloroethylene (TCE) adsorption on granular activated carbon (GAC) from synthetic groundwater. The work starts from an experimental analysis aimed at the assessment of the influence of thermodynamic parameters (concentration, pH, salinity, temperature and the presence of an organic non-ionic compound, i.e. ethyl acetate) on TCE adsorption capacity. A wide range of process parameters have been considered to simulate highly polluted groundwater, as when leachate infiltrations occur at solid waste landfill.

Experimental results show that adsorption capacity decreases by increasing the temperature and the ethyl acetate concentration, while neither pH nor salinity have any influence.

A thorough understanding of adsorption mechanism and the individuation of the model with highest physical and mathematical significance is carried out by a thermodynamic analysis and a statistical methodology based on Analysis of Variance (ANOVA). The latter indicates that in dilute solutions the Freundlich model is the best data fitting model for TCE adsorption, among those which are commonly adopted.

1. Introduction

Groundwater contamination is a worldwide threat for environment and living beings and trichloroethylene (TCE) can be considered as one of the most dangerous and toxic organic pollutants [1,2]. TCE is present in groundwater with concentration as high as few ppm's, as reported by the Environmental Protection Agency in U.S.A. [1,2] and the European Chemicals Bureau in Europe [3]. TCE groundwater contamination derives mainly from industrial discharges, as a result of the manufacturing activity itself, the use, storage and disposal, and from solid waste landfill leachate infiltrations [1,2,4].

Among the depuration technologies for groundwater remediation, adsorption has been widely used because it conjugates good efficiencies with a reliable and robust process configuration.

The most used sorbents for TCE-polluted waters are by far activated carbons [5–9].

Most experimental studies have been focused on how the activated carbon properties influence the TCE adsorption capacity. In particular, several authors [6,9,10] suggested that the optimal carbon pore width ranges for TCE molecule adsorption is typically between 5 and 10 Å, while Li et al. [9] demonstrated that activated carbons with a low oxygen and nitrogen content are the most effective for TCE removal from aqueous solutions.

Pelech et al. [11] analysed the competition effects exert by the presence of other organic compounds. In particular, they observed that the co-presence of chlorinated compounds such as chloroform, carbon tetrachloride, 1,2-dichloroethane, 1,1,2,2-tetrachloroethane, 1,1-dichloroethylene and tetrachloroethylene determines a reduced TCE adsorption capacity. Similarly, the presence of NOM in water solution significantly reduces the efficiency of activated carbon processes due both to a direct site competition on carbon surface and a carbon pore blockage mechanism [8,10]. The influence of ions presence in solution on TCE adsorption is still a debated subject. As a general belief, pH and ionic strength do not affect uncharged organic compounds adsorption on activated carbon [12–15], but a couple of experimental works, focused on TCE adsorption, seems not to follow this general trend. For instance, Kilduff and Karanfil [7] pointed out that the increasing concentrations

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Nomenclature

ω	activated carbon adsorption capacity (mg g^{-1})
$\omega_{\max}$	maximum adsorption capacity (mg g^{-1})
C	liquid concentration (μg l^{-1} or mol l^{-1})
C_{TCE}	TCE equilibrium concentration (μg l^{-1})
K_h	ethyl acetate hydrolysis constant, $2.47 \cdot 10^{-10}$ s^{-1}
T	absolute temperature (K)
R	universal gas constant, 8.314 kJ (mol K)$^{-1}$
ΔH	isosteric heat of adsorption (kJ mol^{-1})
R^2	coefficient of determination
T-test	*T*-Student statistical test
F-test	*F*-Fisher statistical test
P-test	normality test
ResSS (σ^2_{res})	residual sum of squares for the individual observations
LofSS (σ^2_{lof})	lack-of-fit sum of squares for fitting the averages of replica
ErrSS (σ^2_{err})	pure-error components sum of squares
ResDF (ν_{lres})	degrees of freedom for residual sum of squares
LofDF (ν_{lof})	degrees of freedom for lack-of-fit sum of squares
ErrDF (ν_{lerr})	degrees of freedom for pure error sum of squares
ω_{ji}	experimental observation of adsorption capacity, indexed by their predictor variable levels and number of replicate measurements (mg g^{-1})
$\hat{\omega}_j$	adsorption capacity regression responses (mg g^{-1})
$\bar{\omega}_j$	mean of the replicated experimental observations of the adsorption capacity at the *j*th combination of predictor variable levels (mg g^{-1})
k	total number of experimental observations
m	number of unique combinations of predictor variable levels
n_j	number of replicated observations at the *j*th combination of predictor variable levels
p	number of unknown parameters in the model formulation
ResMS	residual mean squares
LofMS	lack-of-fit mean squares
ErrMS	pure error mean squares

of mono and divalent ions (i.e. Na$^+$, Cl$^-$, Ca^{++}) or dissolved oxygen lead to a decrease in TCE adsorption by activated carbon previously loaded with humic substances. Peng and Wan [16] showed that an ionic strength higher than 0.2 M (NaCl) can lead to at least a 10% increase in Henry's constants, favouring the partitioning of TCE into the air phase. More recently, Heo et al. [17] stated that solution ionic strength, mainly by cations, affects TCE adsorption on GAC from synthetic groundwater.

As stated above, TCE adsorption is strongly dependent on chemical GAC properties; in this sense, the solution salinity and the pH alter the carbon superficial charge and then the polarity, resulting in different adsorption properties toward hydrophobic molecules [13,14]. Hence, TCE adsorption could be affected by electrostatic phenomena as well as by pore blockage phenomena deriving by ions adsorption [17]. Moreover, the TCE molecule has a dipole moment that can influences its adsorption on activated carbons immersed in high ionic strength media.

At the same time, groundwater temperature, pH and salinity can vary to a large extent for example when leachate infiltrations occur at solid waste landfill [4,18], and the removal efficiency of adsorption processes can be affected accordingly [12–14,19].

Since literature indications on the effect of the main process parameters on TCE adsorption are not in agreement, a systematic study has been performed. Adsorption tests have been carried out on a commercial granular activated carbon, from synthetic aqueous solutions having chemical composition similar to those frequently found in groundwater. The effect of TCE concentration (0–6 mg l^{-1}), pH (2–12), salinity (0–0.5 M), temperature (10–50 °C), and an organic non-ionic compound concentration (ethyl acetate, 0–0.4 M) have been investigated by a thermodynamic analysis supported by a two level statistical approach. Finally, starting from experimental results, an attempt to a thorough understanding of TCE adsorption mechanism was made, as a first mandatory step for adsorption process optimization.

Table 1
Chemical properties of mineral water used for adsorption tests.

Parameter	Value
pH	8.0
Specific electric conductibility (μS cm^{-1})	242
Salinity (M)	0.0046
[Ca^{++}] (mg l^{-1})	35.9
[Mg^{++}] (mg l^{-1})	12.6
[Na$^+$] (mg l^{-1})	1.9
[HCO_3^-] (mg l^{-1})	149.0
[SO_4^-] (mg l^{-1})	18.6
[Cl$^-$] (mg l^{-1})	2.5

2. Materials

Aquacarb 207EA$^{\mathrm{TM}}$ is a commercially available non impregnated granular activated carbon, produced by Sutcliffe Carbon starting from a bituminous coal. The B.E.T. surface area is 950 m^2 g^{-1} and the average pore diameter is 24 Å. Its chemical composition reveals a high ash content (9.58%) and the value of the pH$_{\mathrm{PZC}}$ = 8.0 shows that the activated carbon has a slightly basic nature.

A complete list of chemical and physical characteristics are reported in Di Natale et al. [20].

In all experimental runs, the aqueous solutions used in the adsorption tests were prepared by adding TCE (Sigma–Aldrich, 99.5%) directly to mineral water, whose main chemical properties (Table 1) are representative of typical groundwater composition [18].

3. Experimentals

Isotherm experiments were conducted in a PID controlled thermostatic oven, using glass vessels as batch reactors. The sample solutions were prepared by adding TCE with a microsyringe (CR-700, Hamilton) and activated carbon to 200 ml amber stained, headspace-free glass vessels of mineral water. The initial solution pH was adjusted by appropriate addition of nitric acid or sodium hydroxide to the stock solutions while the salinity has been modified by adding either inorganic or organic salts, such as sodium chloride, calcium chloride or sodium acetate.

After equilibration, both the TCE concentrations in solution and the TCE adsorbed on the carbon surface have been measured; to such a purpose, the carbon is leached with 200 ml of acetone for a complete TCE extraction, following the EPA methods for soil analysis (EPA 5035). The experimental run accuracy is checked by allowing a maximum error of 8% in the TCE mass balance.

To assure the accuracy, reliability, and reproducibility of the collected data, all batch isotherm tests were performed in triplicate and average values only are reported. Each replica of a repeated test has a TCE concentration variance of the order of 5% while adsorption capacity variance accounts for 4%. Blank tests without sorbent addition, show that the losses in TCE resulting from volatilization, sorption on reactor walls, or photodegradation were less than 2%.

The TCE solution concentrations were measured with a gas chromatograph (Agilent, GC 6890) equipped with an electron capture

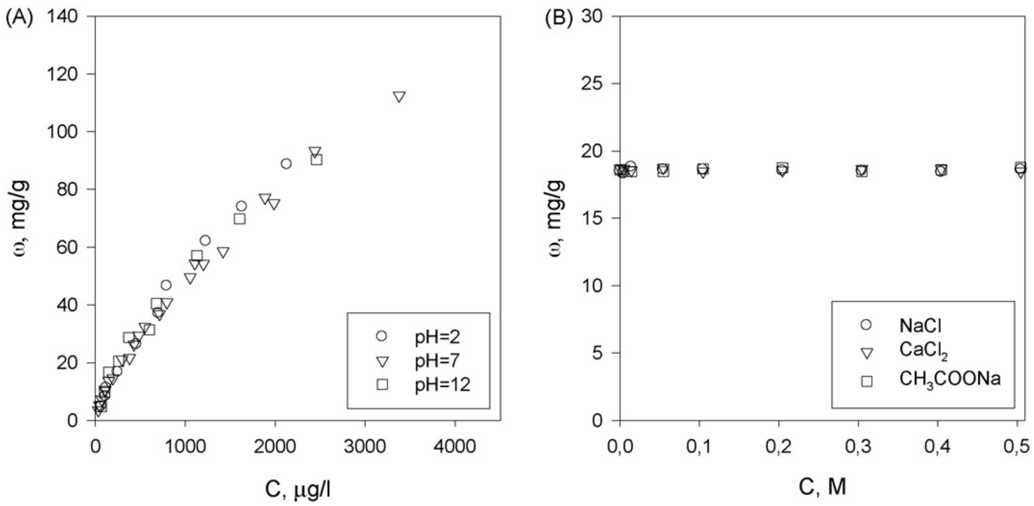

Fig. 1. TCE adsorption capacity onto Aquacarb 207EA^{TM} GAC as a function of pH (A) and salinity (B). $T = 20\,^{\circ}C$.

detector (ECD) and a Purge & Trap system (Tekmar LSC-2000). Analytical methods comply with the EPA method 5030B.

4. Results and discussion

4.1. Experimental results

The effect of concentration and pH on TCE adsorption at 20 °C is reported in Fig. 1A. The TCE adsorption capacity values are typical of activated carbons [4–6,8]; they increase with equilibrium concentration but an asymptotic value is not reached in the investigated range. Moreover Fig. 1 shows that TCE adsorption capacity does not depend on pH values as the slight differences between adsorption capacities are within the variability of TCE concentration experimental measurements (<5%).

The effect of solution salinity on TCE adsorption capacity, obtained by addition, alternatively, of inorganic (NaCl, $CaCl_2$) or organic (CH_3COONa) salt to the TCE solutions, is reported in Fig. 1B. This effect was studied in three different run tests, each of which considering eight samples containing the same TCE initial concentration and the same activated carbon dosage. Then, different salt amounts were added to each sample to reach the desired salinity level. Experimental results, reported in Fig. 2A, show that the TCE adsorption capacity does not depend on salinity regardless of the nature of the added salt, even if its concentration is orders of magnitude higher than that of TCE.

Since there are no effects related with the presence of ions in solution, the effect of the presence of a non-ionic organic compound have been investigated. In Fig. 2B the effect of ethyl acetate ($CH_3COOC_2H_5$) – a commonly used organic solvent – is reported. As for the previous test, different amounts of ethyl acetate (Sigma–Aldrich, 99.5%) were added to seven samples having the same activated carbon dosage and the same initial TCE concentration. In Fig. 2B, the circles indicate the TCE adsorption capacity and equilibrium concentration, together with the indication of the ethyl acetate concentration of the same sample. As can be observed, TCE adsorption capacity is almost constant by increasing both TCE and ethyl acetate concentration. In order to show the occurrence of competition effects between TCE and ethyl acetate, in Fig. 2B the TCE adsorption capacity values obtained in absence of ethyl acetate (triangles) are also reported (values taken from Fig. 1A). As can be observed, TCE adsorption capacity values in presence of ethyl acetate (circle) are generally considerably lower than the corresponding values obtained in absence of ethyl acetate (triangles), both evaluated at the same TCE equilibrium concentration and temperature so that the comparison makes sense. In this way, the results clearly show that the TCE adsorption capacity is greatly influenced by ethyl acetate presence. The extent of the competition effect increases with ethyl acetate concentration; moreover it depends on ethyl acetate adsorption capacity, whose determination is beyond the aim of this work. It is worth noticing that for the pH conditions adopted, the ethyl acetate is unreactive, since its hydrolysis constant is $K_h = 2.47 \cdot 10^{-10}\ s^{-1}$ [21].Organic ($C_2H_3COO^-$) and inorganic ions (Ca^{++}, Na^+, Cl^-), as well as H^+ and OH^- ions, can be significantly adsorbed by activated carbons [14,17,22,23]. However their interference on TCE adsorption (Figs. 1A and B, and 2A) is negligible, as it seems to be affected only by the presence of an organic non-ionic species (Fig. 2B). These results suggest that TCE adsorption mechanism does not involve ionic interactions between TCE and carbon as well as sorbent ionization phenomena. Consequently, TCE molecules and ionic compounds are likely to be adsorbed on different active sites.

An overview of the experimental results, leads to the conclusion that TCE adsorption can be related only to non-specific dispersion interactions (i.e. London-Van Der Walls forces). Actually, these forces can be exerted between delocalized π-electrons of the condensed polyaromatic carbon sheets, acting like Lewis bases and having nucleophilic character [9,24], and the double bond of the TCE molecule that, due to chlorine presence, results highly oxidized and with an electrophilic character [2,25]. These results are consistent with the observations by Karanfil and Dastgheib [6] and Li et al. [9], who stated that TCE adsorption is higher for less oxidized and less acidic surface adsorbents, because the hydrophobic character of carbon is enhanced and the water competitive adsorption is less marked. According to these results, only compounds having this kind of interactions with the carbon surface can be considered as potential TCE adsorption competitors.

Starting from experimental data, a deeper analysis of TCE adsorption dynamics requires the determination of the isosteric heat of adsorption (ΔH). To this aim TCE adsorption isotherms at different temperature levels and pH 7 have been also determined (Fig. 2A). As expected, the adsorption capacity decreases with temperature, in agreement with the exothermicity of adsorption phenomena.

4.2. Thermodynamic analysis

A thermodynamic analysis of the TCE adsorption phenomena has been extended to the measurement of the heat of adsorption

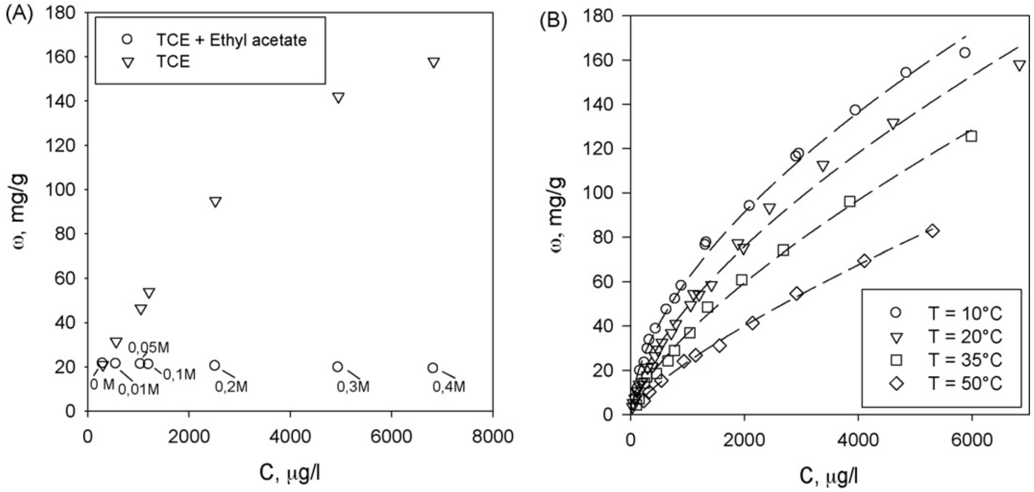

Fig. 2. TCE adsorption isotherm at $T = 20\,^{\circ}\mathrm{C}$ as a function of ethyl acetate concentration (circles) and in monocomponent system (triangle) (A) and TCE adsorption isotherms as a function of temperature (B).

magnitude and its variation with surface loading, as it can provide useful indications on the nature of the carbon surface and the adsorbed phase interactions. The heat of adsorption determined at constant amounts of sorbate adsorbed is commonly known as the "isosteric heat of adsorption" or "differential heat of adsorption" (ΔH), and it is expressed in joules per mole of adsorbate. It is defined as the ratio of the infinitesimal change in the adsorbate enthalpy and the infinitesimal change in the amount adsorbed [12].

The isosteric heat for TCE adsorption can be calculated from the following thermodynamic relationship derived from the Van't Hoff equation [12,26]:

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

The TCE equilibrium concentrations (C) at constant amount of adsorbed TCE (ω) are taken from the adsorption isotherm 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 adsorbed TCE (see Eq. (1)). The ΔH values are shown in Fig. 3 as a function of the TCE surface loadings.

As shown in Fig. 3, the isosteric heat of adsorption decreases by increasing the surface loading with an exponential decay, indicating either the energetic heterogeneity of adsorption sites towards TCE adsorption or the presence of lateral interactions between TCE molecules adsorbed on carbon surface [26], even if, at moment, it is hard to discriminate between them. It can be hypothesized that a strong sorbent–solute interaction takes place initially at lower coverage degrees, resulting in high heat of adsorption, while sorbate–solute lateral interactions occur when the surface coverage increases. These results are consistent with the hypothesis of TCE adsorption on the carbon basal plane, as previously reported. Moreover, they indicate that the Langmuir model is not reliable for the data interpretation because of its intrinsic isoenergetic adsorption sites hypothesis that does not match real TCE adsorption mechanisms. Hence, other models, instead of the Langmuir's, are expected to be more suitable for the analysis of TCE adsorption data.

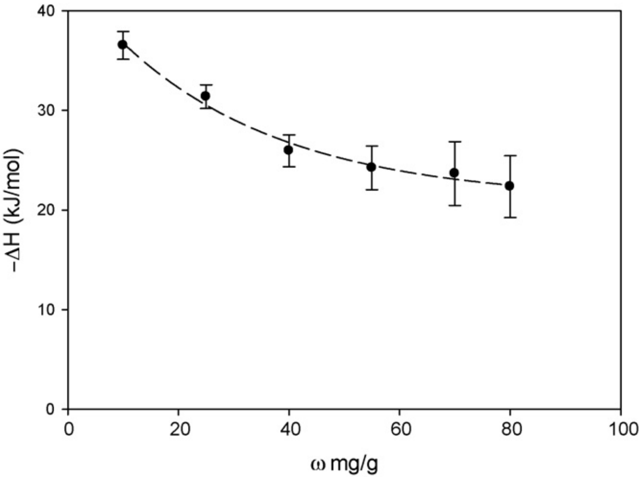

Fig. 3. Isosteric heat of adsorption (ΔH) as a function of surface loadings (ω) for TCE adsorption on GAC. Error bars represent error propagation of C experimental determination error.

4.3. Adsorption isotherm models: statistical analysis

A great number of adsorption models are available in the scientific literature, each one being characterized by a different assumption on the physical phenomenon which prevails over the others [12]. Even if organic compounds adsorption is believed to be based on a micropore filling mechanism [12,27], in dilute systems the adsorption isotherm equations commonly used to describe the experimental data for TCE adsorption are those developed by Freundlich [5,8,11,27], Langmuir [11,28], Langmuir–Freundlich [8,11] models of Dubinin–Radushkevich (DR), and Dubinin–Astakhov (DA) developed from the Polanyi theory [7,27].

In order to analyse this aspect thoroughly and to identify the model that better describes TCE adsorption on GAC, several models [12] have been tested for the experimental data fitting by using a two levels statistical analysis. The first level takes into account the nonlinear least-squares regression analysis, while the second level considers the analysis on regression residuals of each model, and is commonly referred to as lack-of-fit test [30].

In the first level statistical analysis, the least residual sum of squares (ResSS) was used as a criterion for the best fitting parameters of each model. All the regression analyses were carried out on the unmodified isotherm equations, rather than their linearized formulation. This approach is generally considered as the most appropriate [14,30]. The isotherm equations and the model parameters from TCE adsorption regression analysis at $T = 20\,^{\circ}\mathrm{C}$, taken as example from Fig. 1A, are reported in Table 2. The analysis included the mean value and standard error in the determination of the parameters, the coefficient of determination (R^2), the T-test for each parameter, the normality P-test and the F-test for the regres-

Table 2
Isotherm equations and model parameters from TCE adsorption regression analysis at $T = 20\,^{\circ}\mathrm{C}$.

Isotherm	Equation	Parameter	Value			R^2	*P*-test	*F*-test
			Mean	Std error	*T*-test			
Henry	$\omega = H \cdot C$	$H\ (\mathrm{l\,g^{-1}})$	35.02	1.58	22.1	0.8915	<0.0001	180
Temkin	$\omega = B \cdot \ln(KC)$	$K\ (\mathrm{l\,mol^{-1}})$	$1.64 \cdot 10^6$	$3.63 \cdot 10^5$	4.5	0.8320	<0.001	104
		$B\ (\mathrm{mg\,g^{-1}})$	23.46	2.30	10.2			
Freundlich:	$\omega = k \cdot C^n$	$K\ (\mathrm{mg\,g^{-1}})/(\mathrm{\mu g\,l^{-1}})^n$	0.436	0.037	11.7	0.9964	<0.0001	5954
		n	0.680	0.011	70.8			
Langmuir:	$\omega = \frac{\omega_{\max} K \cdot C}{1 + K \cdot C}$	$\omega_{\max}\ (\mathrm{mg\,g^{-1}})$	238.7	13.32	25.1	0.9928	<0.0001	2899
		$\Delta G\ (\mathrm{kJ\,mol^{-1}})$	−25.39	0.21	118.8			
		$K\ (\mathrm{l\,mol^{-1}})$	$33.78 \cdot 10^3$	$2.97 \cdot 10^3$	12.2			
Langmuir–Freundlich:	$\omega = \frac{\omega_{\max} (K \cdot C)^n}{1 + (K \cdot C)^n}$	$\omega_{\max}\ (\mathrm{mg\,g^{-1}})$	596.3	194.7	3.1	0.9975	<0.0001	3929
		$\Delta G\ (\mathrm{kJ\,mol^{-1}})$	−21.06	3.53	5.9			
		$K\ (\mathrm{l\,mol^{-1}})$	$5.69 \cdot 10^3$	$3.43 \cdot 10^3$	1.7			
		n	0.771	0.035	21.9			
Toth	$\omega = \frac{\omega_{\max} K \cdot C}{(1 + (K \cdot C)^n)^{1/n}}$	$\omega_{\max}\ (\mathrm{mg\,g^{-1}})$	$13.26 \cdot 10^3$	$31.60 \cdot 10^3$	0.42	0.9972	<0.0001	3594
		$\Delta G\ (\mathrm{kJ\,mol^{-1}})$	−19.11	−1.93	9.9			
		$K\ (\mathrm{l\,mol^{-1}})$	$2.58 \cdot 10^3$	$4.09 \cdot 10^3$	0.63			
		n	0.214	0.096	2.2			
Dubinin–Radushkevich:	$\omega = \omega_{\max} \exp\left[-\left(\frac{RT}{E} \ln\left(\frac{c_s}{c}\right)\right)^2\right]$	$\omega_{\max}\ (\mathrm{mg\,g^{-1}})$	594.7	22.9	26.0	0.9959	<0.0001	5140
		$E\ (\mathrm{kJ\,mol^{-1}})$	10.68	0.10	105.9			
Dubinin–Astakhov:	$\omega = \omega_{\max} \exp\left[-\left(\frac{RT}{E} \ln\left(\frac{c_s}{c}\right)\right)^n\right]$	$\omega_{\max}\ (\mathrm{mg\,g^{-1}})$	1450.1	590.0	2.5	0.9972	<0.0001	3596
		$E\ (\mathrm{kJ\,mol^{-1}})$	7.11	1.41	5.1			
		n	1.42	0.19	7.6			

Table 3
Results of lack-of-fit test for adsorption models analysis.

Model	ResSS (σ^2_{res})	ResDF (ν_{res})	LofSS (σ^2_{err})	LofDF (ν_{lof})	ErrSS (σ^2_{lof})	ErrDF (ν_{err})	$F_{\upsilon_{\mathrm{lof}},\upsilon_{\mathrm{err}}} = \frac{\sigma^2_{\mathrm{lof}}/\upsilon_{\mathrm{lof}}}{\sigma^2_{\mathrm{err}}/\upsilon_{\mathrm{err}}}$	$F(0.05)_{\nu_{\mathrm{lof}};\nu_{\mathrm{err}}}$; $F(0.01)_{\nu_{\mathrm{lof}};\nu_{\mathrm{err}}}$
Freundlich:	1163	58	596	23	566	35	1.60	1.84; 2.38
Langmuir:	1830	58	1263	23	566	35	3.39	1.84; 2.38
Langmuir–Freundlich:	1302	57	736	22	566	35	2.07	1.85; 2.40
Toth	1275	57	709	22	566	35	1.99	1.85; 2.40
Dubinin–Radushkevich:	1282	58	715	23	566	35	1.92	1.84; 2.38
Dubinin–Astakhov:	1193	57	626	22	566	35	1.76	1.85; 2.40

sion. The meanings of these parameters are reported in classical statistical works [31].

The regression analysis of experimental data at 20 °C shows that for each model the coefficient of determination (R^2) is very high, except for Henry and Temkin models that, for this reason, have been dismissed. The *T*-test, as the ratio of the regression coefficient to its standard error, shows a low accuracy in parameters prediction for Langmuir–Freundlich, Toth and Dubinin–Astakhov models.

As discussed before, the analytical methods, the theoretical tools and the basic statistical analyses cannot help to define the real adsorption mechanism among those cited and then they cannot provide the best fitting model. Hence, a second level statistical analysis has been carried out through an Analysis of Variance (ANOVA) on regression residuals of each model, commonly referred to as lack-of-fit test for model adequacy [30]. 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 and pure error components sum of squares (ErrSS), which account for variations in the replicated response values at the same point. This method can be used only when data points are replicated. The details of the lack-of-fit test are reported in Appendix A.

The cut-off values from published *F*-tables (named $F(0.05)_{\nu_{\mathrm{lof}};\nu_{\mathrm{err}}}$ and $F(0.01)_{\nu_{\mathrm{lof}};\nu_{\mathrm{err}}}$) are reported in Table 3 [32], as a function of LofSS and ErrSS degrees of freedom (LofDF and ErrDF, respectively), and together with the results of the lack-of-fit test. In this paper, the significance levels have been set to 95% and 99%, so that there is only 5% and 1% probability, respectively, of exceeding the published *F*-values through random fluctuations in the data.

The lack-of-fit test clearly shows that the Langmuir model is inadequate at a 99% confidence level; this confirms the indication resulting from the isosteric heat of adsorption analysis, as reported in Section 4.2. Moreover, the results show that at a 95% confidence level the only models adequate to describe the experimental data are Freundlich and Dubinin–Astakhov, even if the latter shows a bigger statistical uncertainty (cfr. Table 2), probably due to a higher number of parameters. Hence, in dilute solutions, the Freundlich model shows the greater affinity with the adsorption mechanism and the experimental data at different temperatures, as testified in Fig. 1A. This result confirms the indication of Kleineidam et al. [27] working over a wider range of TCE concentration. Moreover, the three-parameter Dubinin–Astakhov model could be more suitable in a higher range of concentrations [7,27].

5. Conclusions

In this work an experimental analysis of trichloroethylene adsorption on GAC from synthetic aqueous solutions having chemical composition similar to groundwater has been carried out. The adsorption capacity decreases with temperature, according to the exothermicity of adsorption phenomena, while neither salinity nor pH have any influences. A competitive effect can be exerted only by an organic non-ionic species. TCE adsorption mechanism does not involve ionic interactions between solid and solute and it seems to be related to electrostatic interactions between delocalized π-electrons of the condensed polyaromatic carbon sheets, acting like Lewis bases and having nucleophilic basic character, and the highly oxidized TCE molecule double bond due to the chlorine atoms presence, having electrophilic character.

A thermodynamic analysis on adsorption process has been extended to the measurement of the isosteric heat of adsorption, showing that it depends on the TCE surface loading, with an exponential decay trend. It indicates either the energetic heterogeneity of adsorption sites towards TCE adsorption or the presence of lateral interactions between TCE molecules adsorbed on carbon surface. Hence, other models, instead of the Langmuir's, seems to have the higher physical meaning for TCE adsorption interpretation.

A two levels modelling statistical analysis has been performed on the experimental data set showing that only the second level, based on ANOVA analysis on regression residuals of each model (lack-of-fit test), allows the definition of models reliability. This analysis has indicated that, for the dilute solutions considered in this work, the Freundlich model is the best data fitting model for TCE adsorption.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2009.10.034.

References

[1] Agency for Toxic Substances and Disease Registry (ATSDR), Toxicological profile for trichloroethylene (TCE). U.S. Public Health Service, U.S. Department of Health and Human Services, Atlanta, GA., 1997.

[2] EPA (U.S. Environmental Protection Agency), TCE removal from contaminated soil and groundwater, EPA/540/S-92/002, 1992.

[3] ECB (European Chemicals Bureau), European union risk assessment report: vol 31 - Trichloroethylene part 1 (Environment), European Commission, 2005.

[4] P. Kjeldsen, M.A. Barlaz, A.P. Rocker, A. Baun, A. Ledin, T.H. Christensen, Present and long-term composition of MSW landfill leachate: a review, Crit. Rev. Env. Sci. Technol. 32 (4) (2002) 297–336.

[5] K. Urano, E. Yamamoto, M. Tonegawa, K. Fujie, Adsorption of chlorinated organic compounds on activated carbon from water, Water Res. 25 (12) (1991) 1459–1464.

[6] T. Karanfil, S. Dastgheib, Trichloroethylene adsorption by fibrous and granular activated carbons: aqueous phase, gas phase, and water vapour adsorption studies, Environ. Sci. Technol. 38 (2004) 5834–5841.

[7] J.E. Kilduff, T. Karanfil, Trichloroethylene adsorption by activated carbon preloaded with humic substances: effects of solution chemistry, Water Res. 36 (2002) 1685–1698.

[8] J.E. Kilduff, T. Karanfil, W.J. Weber, Competitive effects of nondisplaceable organic compounds on trichloroethylene uptake by activated carbon. I. Thermodynamic predictions and model sensitivity analyses, J. Colloid Interface Sci. 205 (1998) 271–279.

[9] L. Li, P. Quinlivan, D.R. Knappe, Effects of activated carbon surface chemistry and pore structure on the adsorption of organic contaminants from aqueous solution, Carbon 40 (2002) 2085–2100.

[10] P. Quinlivan, L. Li, D.R. Knappe, Effects of activated carbon characteristics on the simultaneous adsorption of aqueous organic micropollutants and natural organic matter, Water Res. 39 (2005) 1663–1673.

[11] R. Pelech, A. Bembnowska, E. Milchert, Adsorption of hydrocarbon chloroderivatives onto DTO commercial carbon from multi-component aqueous solutions, Adsorpt. Sci. Technol. 21 (8) (2003) 707–720.

[12] D.D. Do, Adsorption Analysis: Equilibria and Kinetics, Imperial College Press, London, 1998.

[13] C. Moreno-Castilla, Adsorption of organic molecules from aqueous solutions on carbon materials, Carbon 42 (2004) 83–94.

[14] M. Benjamin, Water Chemistry, McGraw Hill, New York, 2002.

[15] S. Mukherjee, S. Kumarb, A.K. Misra, M. Fan, Removal of phenols from water environment by activated carbon, bagasse ash and wood charcoal, Chem. Eng. J. 129 (2007) 133–142.

[16] J. Peng, A. Wan, Effect of ionic strength on Henry's constants of volatile organic compound, Chemosphere 36 (13) (1998) 2731–2740.

[17] J.H. Heo, D.H. Lee, D.C. Koh, H.W. Chang, The effect of ionic strength and hardness of trichloroethylene-contaminated synthetic groundwater on remediation using granular activated carbon, Geosci. J. 11 (3) (2007) 229–239.

[18] A. Zaporozec (Ed), Groundwater Contamination Inventory: A Methodological Guide IHP-VI, Series on groundwater No 2, UNESCO, Paris, France, 2002.

[19] D. Kalderis, D. Koutoulakis, P. Paraskeva, E. Diamadopoulos, E. Otal, J. Olivares del Valle, C. Fernandez-Pereira, Adsorption of polluting substances on activated carbons prepared from rice husk and sugarcane bagasse, Chem. Eng. J. 144 (2008) 42–50.

[20] F. Di Natale, A. Erto, A. Lancia, D. Musmarra, Experimental and modelling analysis of As(V) ions adsorption on granular activated carbon, Water Res. 42 (8–9) (2008) 2007–2016.

[21] -C.H. Bramford, C.F.H. Tipper, Comprehensive Chemical Kinetics, vol. 10, Elsevier, Amsterdam, 1972.

[22] A. Alfarra, E. Frackowiak, F. Béguin, The HSAB concept as a means to interpret the adsorption of metal ions onto activated carbons, Appl. Surf. Sci. 228 (2004) 84–92.

[23] D. Mugisidi, A. Ranaldo, J.W. Soedarsono, M. Hikam, Modification of activated carbon using sodium acetate and its regeneration using sodium hydroxide for the adsorption of copper from aqueous solution, Carbon 45 (5) (2007) 1081–1084.

[24] C.A. Leon y Leon, J.M. Solar, V. Calemma, L.R. Radovic, Evidence for the protonation of basal plane sites on carbon, Carbon 30 (5) (1992) 797–811.

[25] T.W.G. Solomons, C.B. Fryhle, Organic Chemistry, eighth ed., John Wiley & Sons Hoboken, New Jersey, 2004.

[26] M. Suzuki, Adsorption Engineering, Elsevier, Amsterdam, 1990.

[27] S. Kleineidam, C. Schuth, P. Grathwohl, Solubility-normalized combined adsorption-partitioning sorption isotherms for organic pollutants, Environ. Sci. Technol. 36 (2002) 4689–4697.

[28] J. Li, C.J. Werth, Modeling sorption isotherms of volatile organic chemical mixtures in model and natural solids, Environ. Toxicol. Chem. 21 (7) (2002) 1377–1383.

[29] A. Bembnowska, R. Pelech, E. Milchert, Adsorption from aqueous solutions of chlorinated organic compounds onto activated carbon, J. Colloid Interface Sci. 265 (2003) 276–282.

[30] D.C. Montgomery, Design and Analysis of Experiments, fifth ed., John Wiley & Sons Inc, New York, 2001.

[31] A. Hald, Statistical Theory With Engineering Applications, John Wiley & Sons Inc., New York, 1952.

[32] D.B. Owen, Handbook of Statistical Tables, Addison Wesley publishing Co, Massachusetts, 1962.

[33] T.J. Zielinski, R.D. Allendoerfer, Least squares fitting of nonlinear data in the undergraduate laboratory, J. Chem. Educ. 74 (8) (1997) 1001–1007.