# Fixed-bed Adsorption of Trichloroethylene onto Activated Carbon

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The present work deals with the study of the adsorption of Trichloroethylene (TCE) onto a commercial granular activated carbon (GAC). Thermodynamic (batch) and dynamic (fixed-bed column) tests were carried out, under a wide range of operating conditions. In particular, adsorption isotherms were preliminary determined to support the investigation on a fixed-bed column at lab-scale. The main fluid dynamic and physical parameters such as flow rate, TCE concentration and GAC particle size were investigated.

Experimental data on fixed-bed column show that an increase in TCE initial concentration and, more markedly, an increase in flow rate lead to a shorter breakpoint time. In fact, the breakthrough curves become steeper as a consequence of higher velocity that enhances the external mass transport.

Finally, a thorough modeling analysis of the fixed-bed column was carried out using a model that includes axial dispersion and external-film diffusion followed by internal diffusion. A good accordance between experimental data and model results was observed.

## 1. Introduction

The presence of chlorinated organic compounds in natural water and subsurface aquifers represents a serious human health threat, due to the persistence, diffusion and accumulation phenomena. Based on a combined evaluation of frequency, toxicity and potential for human exposure, Trichloroethylene (TCE) is considered at the top of the list of hazardous substances (ATSDR, 1997).

The remediation of TCE contaminated aquifers can be carried out alternatively by air stripping, advanced oxidative processes, reductive dechlorination, biological processes and adsorption (EPA, 1992; Benjamin, 2002). In particular, adsorption process can be considered an optimal strategy to remove pollutants of different nature from waters and wastewaters, including TCE, due to its good removal efficiencies and to its great versatility (Li et al., 2002; Erto et al., 2009).

Activated carbons are by far the most used sorbents for TCE removal (Erto et al., 2010a); moreover the treatment can be performed either in-situ, performed with Permeable Adsorbing Barriers (PAB) (Erto et al., 2011a), or ex-situ, coupled with pump and treat technique and mainly with a fixed-bed column (Pelech et al., 2005).

In any case, the performance of an adsorption treatment mainly depends on the thermodynamic aspects of solute-solvent-sorbent interactions and on the transport phenomena involving the diffusive-convective transport within the porous media (Erto et al., 2010a; Leone et al., 2012).

In our recent work, it was demonstrated that the adsorption capacity of chlorinated organic compounds onto activated carbon mainly depends on temperature and on the competitive interaction with other compounds of similar nature, whereas pH and salinity seem to exert a negligible effect (Erto et al., 2011b).

In a fixed-bed device, the contaminated water is introduced in a clean bed of activated carbon from the top and pollutant removal occurs in a narrow band at the top of the column, referred to as mass transfer zone (MTZ). As operation proceeds, the upper layers of activated carbon become saturated with solute and the adsorption zone moves downward until the bottom of the column is reached. Under these conditions, the

solute concentration in the effluent begins to increase. The MTZ extent mainly depends on liquid-solid relative velocity, and on adsorbent properties (particle diameter, microporous structure); as well known in the literature, the higher the MZT extent the lower the efficiency use of the adsorbing bed.

The influence of these parameters on activated carbon performances for TCE adsorption, both from a thermodynamic and a kinetic point of view, are not clarified.

The present work deals with an experimental analysis of the adsorption of TCE onto a commercial granular activated carbon, inclusive of a thermodynamic (i.e. adsorption isotherm determination) and a kinetic analysis (i.e. dynamic tests). Adsorption isotherms were preliminary determined to support the investigation on a fixed-bed column at lab-scale. The main fluid dynamic and physical parameters such as flow rate and pollutant concentration were investigated, in order to determine their effect on the overall adsorption rate. This information is commonly considered as fundamental for a proper device scale-up, for a cost-effective adsorption column design and for a general process optimization.

Finally, a thorough modeling analysis of the fixed-bed column was carried out as a support for the design of adsorption units for TCE removal from polluted water.

## 2. Materials and methods

### 2.1 Activated carbon properties

The sorbent used in this work is a granular activated carbon (GAC), Aquacarb 207EA[TM] provided by Sutcliffe Carbon. This material is a commercially available GAC derived from a bituminous coal and activated by steam.

The morphological analysis shows that Aquacarb 207EATM has a BET surface area of 950 $m^2$ $g^{-1}$ and an average pore diameter of around 26 Å. A granulometric range of 0.1-1.4 mm was adopted for particle diameter ($d_p$) in all the experimental tests. The chemical composition of the sorbent was evaluated by elemental analysis, which reveals a typical activated carbon composition and high ash content (9.5 %). Sorbent characterization also included the evaluation of the $pH_{PZC}$ point (=8) and the analysis of surface functional groups by Boehm's titration analysis, which showed a slightly basic character. A complete sorbent characterization was reported in Erto et al. (2010a).

### 2.2 Experimental procedures

In all experimental runs, the aqueous solutions used in the adsorption tests were prepared by adding TCE (Sigma Aldrich, 99,5 %) to an organics-free mineral water having a pH=8 and ionic strength = 0,46 mM. A complete list of chemical properties is reported in Erto et al. (2010b).

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 a constant mass of activated carbon (0.5 g) to 0.2 L amber stained, headspace-free glass vessels of mineral water.

The kinetic study was conducted by using a glass fixed-bed column having an internal diameter ($d_c$) of 0.01 m and a height of 0.2 m. After a preliminary selection, a cut grain size of GAC in the range 0.1-0.2 mm (average particle diameter, $d_p$) was selected. A constant amount (0.25 g) of activated carbon was used for all the experimental runs in fixed-bed column, corresponding to a height of 0.01 m. The remaining free space of the column was filled up with glass spheres of the same dimension of GAC, both under the activated carbon in order to support the bed and over the GAC bed, to assure an equally distributed flux passing through the bed itself.

TCE solution was fed to the fixed-bed column in downward direction in order to avoid any handling of the GAC fixed-bed. A flow rate varying between 5 and 20 mL $min^{-1}$ was adopted. TCE concentration was varied in the range 3-6 mg $L^{-1}$ and was regularly measured, resulting almost constant during the tests.

The TCE solution concentrations were measured with a gas chromatograph (Agilent, GC 6890) equipped with an electron capture detector (ECD) and a Purge & Trap system (Tekmar LSC-2000). Analytical methods comply with the EPA method 5030B.

## 3. Results and discussion

Figure 1 reports the TCE adsorption isotherm on the 0.1-0.2 mm cut grain of Aquacarb 207EA[TM] GAC, which was shown to be the most appropriate for the dynamic tests reported in the following.

TCE adsorption capacity increased with equilibrium concentration but an asymptotic value was not reached in the concentration range investigated. A comparison with adsorption data previously obtained on the same activated carbon but on 1.18-1.40 mm grain cut, shows that TCE adsorption capacity on Aquacarb 207EA™ is almost independent on GAC particle-size (Erto et al., 2010b).

Moreover, the Freundlich model provided the best fitting for TCE adsorption data as shown in Figure 1, with a coefficient of determination $R^2$=0.989. In the same works, in fact, it was demonstrated that the

interaction between TCE and activated carbon is heteroenergetic, due to the asymmetrical shape of TCE molecules (Erto et al., 2009).
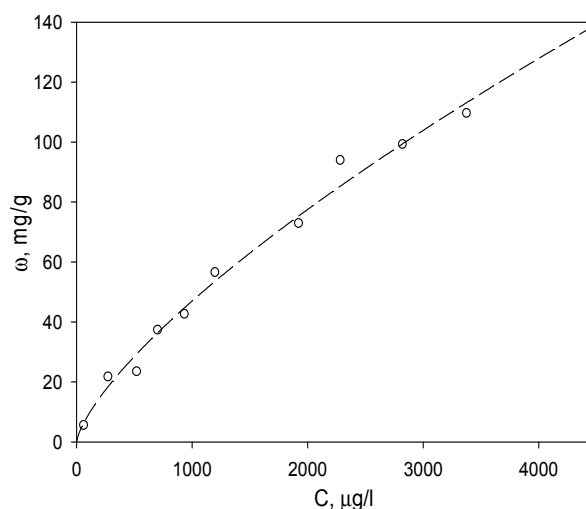


*Figure 1: TCE adsorption capacity onto Aquacarb 207EA™ GAC. ($d_p$=0.1-0.2 mm, T=20 °C). Comparison between experimental data (circles) and Freundlich model (line)*

The TCE adsorption isotherm was obtained to support the experimental and modeling analysis conducted on the lab-scale fixed-bed column.

Preliminary dynamic tests (not reported) showed that the cut grain size of GAC has an effect on TCE mass transport phenomena, as the width of fixed-bed MTZ decreased when the mean particle diameter decreased from 1.4 mm to 0.1 mm. In particular, in correspondence of 0.3-1.4 mm particle diameters, the MTZ was wider than bed height, leading to a greater-than-zero TCE concentration in the effluent in the first instant of the dynamic test. With this result in mind, the adsorbing particle diameter was chosen in the range 0.1-0.2 mm so as to have breakthrough curves adequately developed during the working time (i.e. with normalized concentration values increasing from zero up to one). Moreover, a proper $d_c$ to $d_p$ ratio (≥15) prevents any by-pass phenomena on column walls.

In Figure 2, the dynamic adsorption tests carried out at constant flow rate (Q=10 ml min$^{-1}$) and for different TCE initial concentrations (3-6 mg l$^{-1}$) are reported.

Experimental data show that an increase in TCE initial concentration leads to shorter breakpoint time. For higher TCE concentrations, GAC shows higher adsorption capacity (Figure 1) but a faster GAC coverage rate due to higher TCE concentration seems to predominate.

In Figure 3, the dynamic adsorption tests carried out at constant TCE initial concentration ($C_0$= 3 mg l$^{-1}$) and for different TCE solution flow rates (Q= 5-20 ml min$^{-1}$) are reported.

Results in Figure 3 show that an increase in flow rate determines a more rapid GAC saturation and hence a shorter breakpoint time. Moreover, the breakthrough curves become steeper as a consequence of higher velocity that enhances the external mass transport.

The general model used to predict the fixed-bed dynamics included external film diffusion and intraparticle mass transport, while the stage of intrinsic adsorption (kinetic) on the active sites of adsorbent surface is neglected as it is assumed to be instantaneous (Sotelo et al., 2004).

The hypotheses adopted for model construction are reported in the following (Perry and Green, 2004):
- a plug-flow pattern with axial dispersion (and negligible radial dispersion);
- isothermal process due to the relatively high heat capacity of water;
- the adsorbent particles have an isotropic spherical shape;
- the accumulation of pollutant in the liquid contained in the pores of the adsorbent material is negligible
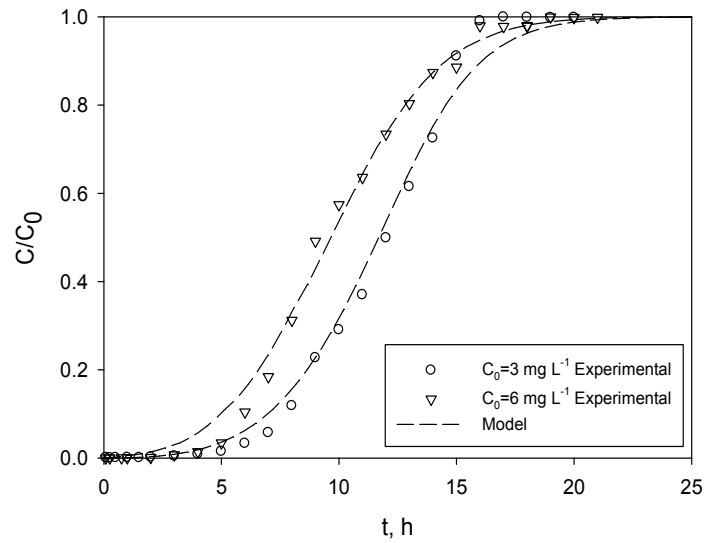- a constant axial velocity.

Figure 2: TCE dynamic adsorption tests onto Aquacarb 207EA™ GAC ($d_p$=0.1-0.2 mm) as a function of TCE initial concentration. T=20 °C, Q=10 mL min$^{-1}$
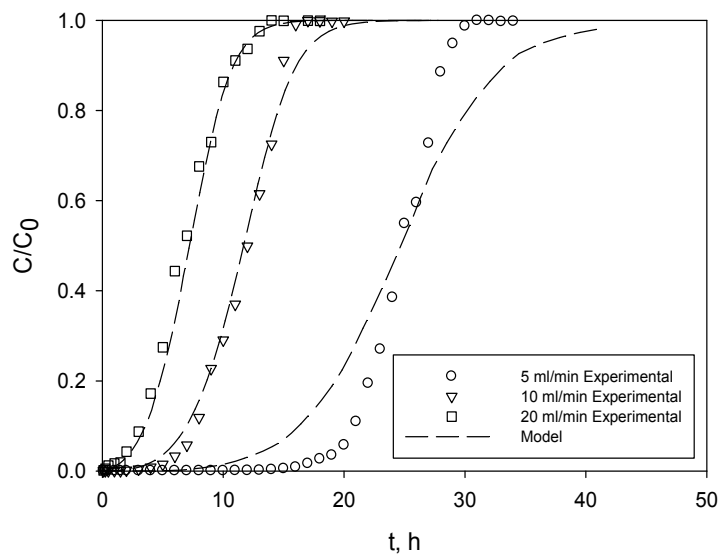


Figure 3: TCE dynamic adsorption tests onto Aquacarb 207EA™ GAC ($d_p$=0.1-0.2 mm) as a function of TCE solution flow rate. T=20 °C, $C_0$=3 mg L$^{-1}$

Under the cited hypotheses, the mass balance equation for the adsorbing system considered can be written as:

$$\varepsilon \cdot \frac{\partial C}{\partial t} + \rho_b \cdot \frac{\partial \omega}{\partial t} = -u \cdot \frac{\partial C}{\partial x} + \varepsilon \cdot D_{ax} \cdot \frac{\partial^2 C}{\partial x^2} \qquad (1)$$

in which:
$u$ is the unit flux vector (apparent velocity) [LT$^{-1}$];
$C$ is the concentration of the contaminant in the fluid flow [ML$^{-3}$].
$\rho_b$ is the apparent density (bulk) of activated carbon [ML$^{-3}$];

$\omega$ is the concentration of pollutant on solid [-];

$D_{ax}$ is the axial diffusivity [$L^2T^{-1}$];

$\varepsilon$ is the porosity of activated carbon bed [-].

The resolution of the equation (1) requires estimating the diffusional mass transport and an experimental relationship that correlates the adsorption capacity of the pollutant with its concentration in the fluid phase (i.e. an adsorption isotherm).

The model includes a transport equation representing the material balance of the solute adsorbed on the solid:

$$\frac{\rho_b}{\varepsilon}\frac{\partial \omega}{\partial t} = k_c a\left[C - C^*(\omega)\right] \tag{2}$$

where:

$a$ is the specific surface area of adsorbent [$L^{-1}$];

$K_c$ is the global mass transfer coefficient [$T^{-1}$];

$C^*$ is the concentration of solute in the liquid phase in equilibrium with the adsorption capacity of solute ($\omega$) [$ML^{-3}$].

The global transport coefficient, $K_c\ a$, can be described as the result of a series of external fluid-particle and intraparticle transport phenomena according to the formula (Perry and Green, 2004):

$$\frac{1}{K_c a} = \frac{1}{K_{est} a_{est}} + \frac{1}{K_{int} a_{int}} \tag{3}$$

where:

$K_{est}$ is the coefficient of external fluid-particle transport;

$K_{int}$, is the diffusive intraparticle coefficient;

$a_{est}$, is the external specific surface particle, being $d_p$ the solid particle average diameter;

$a_{int}$, is the specific surface of solid (i.e. BET area).

There are several non-dimensional relationships in the literature, typically expressed in terms of numbers of Sherwood (*Sh*), Reynolds (*Re*) and Schmidt (*Sc*), for the determination of the term $K_{est}$ (Lancia et al., 1997; Perry and Green, 2004), such as:

$$Sh = 1.85 \cdot \left(\frac{1-\varepsilon}{\varepsilon}\right)^{1/3} \cdot Re^{1/3} \cdot Sc^{1/3} \tag{4}$$

where *Re* represent the particle Reynolds number, defined as:

$$Re = \frac{u\ d_p\ \rho}{\mu} \tag{5}$$

in which:

$\rho$ is fluid density [$ML^{-3}$];

$\mu$ is fluid viscosity [$ML^{-1}T^{-1}$];

$d_p$ is particle diameter [L].

The intraparticle transport coefficient, $K_{int}$, can be expressed as follows (Perry and Green, 2004):

$$K_{int} = \frac{\varepsilon_p D_p}{d_p} \tag{6}$$

in which

$D_p$, is the solute diffusivity in the pores [$L^2T^{-1}$];

$\varepsilon_p$ is particle porosity [-].

In Figures 2-3 model results are included; the comparison between model and experimental results shows that the model provides a very good data interpretation, except for low flow rate in which, probably, the diffusive effects are not negligible, corresponding to a *Re* critical value (<<1). Moreover, the application of the model to the experimental data set showed that the fluid-particle mass transfer coefficient is always

lower than its intraparticle counterpart, so that the mass transfer is limited by the transport in the film fluid surrounding the particle (in particular if the adsorbent particle size is small enough to be the diffusion negligible, as in the present case).

## 4. Conclusions

In this work an experimental analysis of trichloroethylene adsorption on GAC has been carried out. Adsorption isotherms have been carried out, showing that mean particle diameter has a negligible influence on TCE adsorption capacity.

Experimental dynamic tests showed that an increase in TCE initial concentration and in liquid flow rate leads to shorter breakpoint time; moreover, the breakthrough curves become steeper as a consequence of higher velocity that enhances the external mass transport.

An adsorption model was used to predict the fixed-bed dynamics including external film diffusion and intraparticle mass transport, the former resulting the limiting step to overall mass transport in the investigated experimental conditions.

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