Kinetic Features of PCDD Adsorption in Carbon Beds

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Abstract: In this paper, starting from the knowledge of thermodynamic parameters, the adsorption of toxic dioxins is studied in the conditions typically encountered in flue gas treatment processes. The six more poisonous species among all congeners of dioxin group are considered. In particular the theoretical adsorption isotherms are derived and a mathematical tool for planning a feasible fixed bed adsorbers proposed, based on breakthrough and the mass transfer zone curves.

Key-Words: Dioxin, adsorption, activated carbon. kinetics modelling, breakthrough curves, mass transfer zone curves

1 Introduction

Dioxins comprise a wider family of chemical compounds having a similar chemical structure, and namely the poly-chloro-dibenzo-para dioxins (PCDD), dibenzofurans (PCDF) and polychlorodiphenils (PCB). They derive from processes involving chlorine and its derivatives which react with organic matter. The main sources are the combustion processes, mostly those taking place in municipal solid waste incinerators, in paper factories and in factories producing organic and inorganic chlorinated compounds.

The problem of the presence of these organochlorurated micropollutants represents a well-known relevant topic, therefore a great deal of scientific papers has been published, particularly in the field of medicine, where several authors devoted their researches to the comprehension of dioxin formation and to their effects on health [1-3]. On the other hand, very little thermodynamic or kinetic information is available in literature [4-11]. In addition, poor experimental data are at disposal, mainly due to the difficulty encountered in developing a measurement system of these compounds, due to the very small quantities involved (*e.g.* ng or pg).

The mechanism of dioxins formation is well known and a good agreement is found in the specialist literature in considering that a good combustion is essential to hinder the formation of these substances. But even if when combustion conditions are optimal, an adsorption unit in the flue gas treatment line from an incinerator of solid waste is required, in order to realize almost zero dioxins concentration, as imposed by emission regulations.

In order to set up and to run in a proper way an adsorption unit, a scientific approach is required; on the contrary, an empirical approach is very often used, proceeding by trial and error in defining the exact amount of activated carbon to use, in order to achieve the desired PCDD removal, with a not optimized sorbent amount and thus high operating costs.

The purpose of the present paper is to provide a mathematical model, which describes the adsorption breakthrough curves and the mass transfer zone curves of an adsorption unit used to purify the flue gas stream coming from a municipal incineration facility, by taking into account the thermodynamic parameters estimated by the same research group in a previous paper [12].

2 Adsorption Unit Modeling

In this section the planning criteria for dimensioning an activated carbon adsorption unit are given. The mass balance on an element *dx* is to be formulated by taking into account the adsorption kinetic, leading to the following system of partial derivative equations [13-14]:

$$\begin{cases} v\varepsilon \dfrac{\partial C}{\partial x} + \varepsilon \dfrac{\partial C}{\partial t} + (1-\varepsilon)\rho \dfrac{\partial \omega}{\partial t} = 0 \\ \rho \dfrac{\partial \omega}{\partial t} = k_1(\omega_{max} - \omega)\rho C - k_2 \rho \omega \end{cases} \quad (1)$$

The boundary conditions are the following:

$$\begin{cases} t = 0 \quad \text{and} \quad 0 \le x \le L \quad \rightarrow \; C = 0 \; ; \; \omega = 0 \\ t > 0 \quad \text{and} \quad x = 0 \quad \rightarrow \; C = C_0 \end{cases} \quad (2)$$

The equation system has been solved by using the method proposed by Thomas [15], by introducing the following variables:

$$z = \frac{x}{v}$$
$$y = \frac{\varepsilon}{1-\varepsilon}\left(t - \frac{x}{v}\right)$$
$$a = \frac{1\text{-}\varepsilon}{\varepsilon} \cdot k_2 \quad (3)$$
$$\alpha = \rho \omega_{max} K$$

The following analytic solution is obtained:

$$C(x,t) = C_0 \frac{I_0(2a\sqrt{\alpha y z}) + \Phi\left[a(1+KC_0)y, \dfrac{\alpha a z}{1+KC_0}\right]}{I_0(2a\sqrt{\alpha y z}) + \Phi\left[a(1+KC_0)y, \dfrac{\alpha a z}{1+KC_0}\right] + \Phi[\alpha a z, a y]} \quad (4)$$

where I_0 is the modified Bessel function of zero order, $K = k_1/k_2$, and Φ is the following two variables function:

$$\Phi(u,w) = e^u \int_0^u e^{-s} I_0(2\sqrt{ws})ds \quad (5)$$

Table 1. Model parameters for simulation runs

Parameter	*Value*	*Units*
V	0.4	m/s
ε	0.5	-
C_0	6	mg/m^3
ω_{max}	0.7901	-
K	8.59	m^3/g
k_2	6.37·10^{-4}	s^{-1}
ρ	450	kg/m^3

In Table 1 the model parameters, used in some of the simulation runs, are reported. All the thermodynamic parameters used in the simulation runs have been taken from our previous work [12].

3 Results

Figure 1 reports the behaviour of T4CDD concentration as a function of time for different coordinates along adsorber length, and namely 1, 5 and 10 mm from bed entrance; these so called *breakthrough* curves allow to evaluate the time occurring so that the concentration reaches a prefixed value (typically 50% of saturation) in a well-defined coordinate along the bed axis (typically the outlet section).

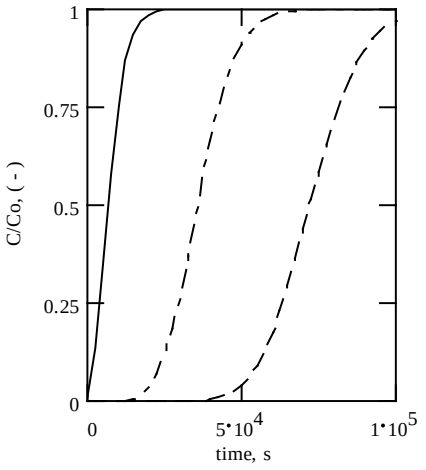

Figure 1. Breakthrough curves for T4CDD; T=433 K; —: 1mm; -·-: 5mm; - - -: 10mm

Figure 2 shows the behaviour of T4CDD concentration as a function of bed length with time as parameter. The curves, noted as *mass transfer zone* (*MTZ*) curves in literature, represent the concentration wave propagation along the bed while increasing the bed operation time. From *MTZ* curves, it is possible to individuate the part of the bed active towards mass transfer.

Particularly, the analysis of Figs 1 and 2 reveals that T4CDD needs about 28 hours to saturate a bed depth of 10 mm (Fig. 1); moreover, the arrival time of concentration wave on this bed coordinate is of about 15 hours (Fig. 2).

Obviously, this analysis holds for a one-component gas, *i.e.* containing the T4CDD molecule only; moreover it demands ideal conditions, by modelling

the carbon bed as a compact layer of adsorbing material.

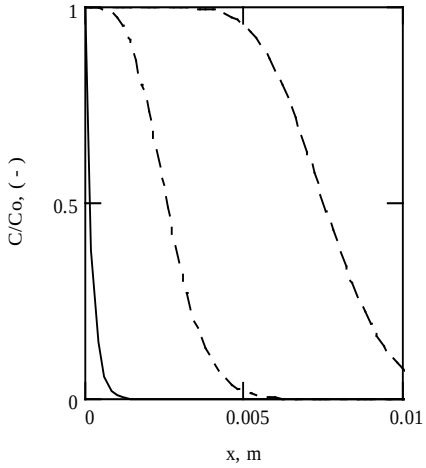

Figure 2. MTZ curves for T4CDD; T=433 K; —: 10 s (0.003 h); -·-: 18000 s (5 h); - - -: 54000 s (15 h)

This situation is very different from that encountered in the industrial practise, where most of all it is necessary to consider the different adsorbing characteristics of the several PCDD, besides all other substances composing an incinerator flue gas, which could alter adsorption phenomena.

The treatment of adsorption from gas mixtures, in particular its modelling, is complex and beyond the scope of this paper. The proposed model is able to simulate the adsorption of a single PCDD molecule, once known its kinetic parameters. For planning an adsorption unit which treats a gas mixture, as for adsorber located in incinerator flue gas treatment scheme, the approach followed by EPA in VOC adsorbing reactors has been considered [16]. In the adsorption of a mixture, competition for available sites occurs, *i.e.* one component will tend to displace another on the carbon surface and generally, molecules with lower vapour pressures will displace those with higher vapour pressure, resulting in the former displacing the latter previously adsorbed. Thus, during the course of the adsorption cycle the carbon's capacity for a higher vapour pressure constituent decreases. To be conservative, when sizing the adsorber, the adsorption cycle requirements should be based on the least adsorbable component in a mixture [16].

According to this consideration, on the basis of the results previously reported [12] that indicate the T4CDD as the less adsorbable PCDD among those studied, the sizing of the bed has been carried out considering exactly the T4CDD.

As a proof of what said, Figure 3 reports the breakthrough curve for H6CDD at the same temperature T=433 K. The figures comparison shows that T4CDD and H6CDD for an adsorbing time of 28 h ($1 \cdot 10^5$ s) saturate a bed length of 10 and 2 mm, respectively.

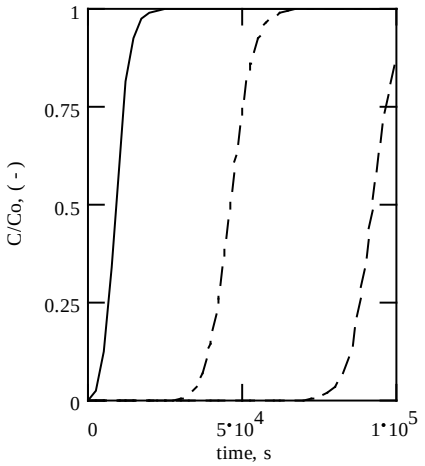

Figure 3. Breakthrough curves for H6CDD; T=433 K; —: 0.2mm; -·-: 1mm; - - -: 2mm.

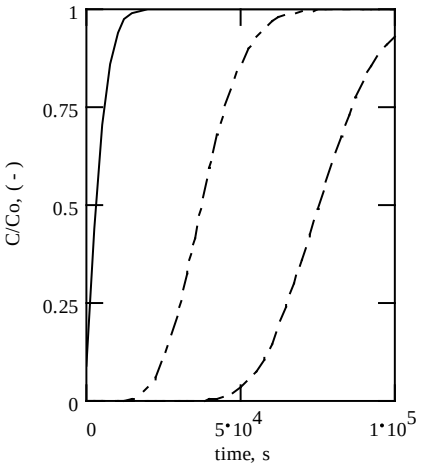

Figure 4. Breakthrough curves for T4CDD, T=493 K; —: 10mm; -·-: 100mm; - - -: 200mm.

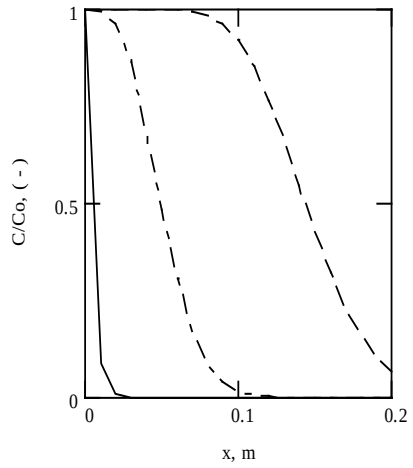

Figure 5. MTZ curves for T4CDD, T=493 K; —: 10 s (0.003 h); -·-: 18000 s (5 h); - - -: 54000 s (15 h).

In Figures 4 and 5 the *breakthrough* and *MTZ* curves for the T4CDD are reported for *T*=493 K.

As well-known from adsorption literature [17], as temperature increases adsorption get worse. As a matter of fact a comparison among Figs. 1-2 (*T*=433 K) and Figs. 4-5 (*T*=493 K), shows a decrease in bed adsorption capacity; particularly, for a time of 28 hours ($1 \cdot 10^5$ s), a bed length twenty times higher get saturated.
Eventually, at the planning stage the kinetic adsorption parameters, together with the programmed working times (adsorption-desorption cycles for bed regeneration) allow to calculate the amount of carbon to put in the bed and, as a consequence, the sizing of the reactor itself.

4 Conclusion

A rational design of an adsorption unit devoted to remove hazardous compounds, such as dioxins and furans, from flue gases coming from incinerators has been presented.
A useful and reliable tool has been tested by the design of a specific process unit, that is an adsorber unit, which could fit in a classical flue gas treatment process scheme. A mathematical model has been proposed, which describes the adsorption breakthrough curves and the mass transfer zone curves. confirms the reliability of the proposed Further works will be devoted to proper design and compare several process units devoted to dioxins removal in order to provide an useful unit performance diagram able to guide the reader towards the right process unit selection based on specific process working conditions..

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