



## ESTIMATION OF DIFFUSIVITY OF MERCURY IN ADDICTIVED ACTIVATED CARBON

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**Abstract.** In this work the diffusivity of mercury in a commercial additived activated carbon was experimentally determined using an Argelian condensate. The diffusivity was estimated using the homogeneous solid diffusion model (HSDM) for short and long times (effective diffusivity). To the employed solid/liquid ratios, the values the diffusivity at short times were smaller than the corresponding values at long times and were in range obtained to diffusivity of organic solutes in activated carbon. The effective diffusivity was found to better represent the process than the diffusivity determined at short times, indicating that diffusivity depends on solute concentration in solid.

**Keywords:** Mercury, Diffusivity, Adsorption.

### 1. Introduction

Crude oil and gas condensate can contain relatively high concentrations of mercury compounds ( $0.01 \mu\text{g.kg}^{-1}$  and  $10 \text{mg.kg}^{-1}$ , Wilhelm and Bloom, 2000). The total mercury concentration can include different chemical forms of mercury such as inorganic ( $\text{Hg}^0$ ,  $\text{HgCl}_2$ ,  $\text{HgS}$ ), organic ( $\text{RHgR}$  and  $\text{RHgCl}$ , where  $\text{R} = \text{CH}_3$ ,  $\text{C}_2\text{H}_5$ , etc) and even complex forms ( $\text{HgK}$ , where  $\text{K} =$  organic sulfide, thiol, thiophene or mercaptano).

In petrochemical processing industries, the presence of Hg is detrimental since it can cause, for example, cracking of welded aluminum heat exchanger, damages in cryogenic equipment, generation of toxic waste, increment of risk to the health and safety of workers and poisoning of catalysts. To protect equipment and environment, it is necessary to reduce the Hg and its compounds content on condensate and crude oil at the smallest possible levels, considering the diversity of feeds used in the petrochemical plants.

Among the available industrial process for the removal of Hg and compounds of Hg from liquid hydrocarbons, the fixed bed adsorption process is one of the most used. The granular or pelletized sorbents of the bed generally consist of a reactive compound (Ag, KI, CuS, metal sulfide, etc) supported on a specific substract (zeolite, activated carbon, metal oxide or alumina), as described by Wilhelm (2001). The solute removal efficiency in the bed depends, mainly, on the overall dynamic of the process, involving the flow rate, the flow pattern, the fluid-to-particle and the intraparticle resistance to mass transfer more than equilibrium considerations, as presented in Geankoplis (1993).

For modeling and projecting industrial fixed bed adsorption systems it is necessary to determine both the external and the intraparticle resistance. The mass transfer rate from the outer surface of the solid to the inner surface of its internal porous structure is characterized by the diffusion coefficient ( $D_s$ ). It can be determined

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through kinetic test data in stirred-batch adsorption experiment. The  $D_s$  value, obtained from these tests, can be used in the modeling of fixed bed adsorber, since the particle size of the adsorbent is the same, as presented in Cooney (1999). In this work, the diffusivity of mercury in a commercial activated carbon is determined through experimental data, using an Algerian condensate. The diffusivity is estimated using the so-called homogeneous solid diffusion model, for short times and for the entire uptake process (effective diffusivity,  $D_{ef}$ ).

## 2. Experimental

The employed materials and methods used to do the batch adsorption tests in this study are described below, as well as, the way of estimating the diffusivity values.

### 2.1. Materials

A commercial activated carbon, impregnated with metal sulfide as reactive component, was used as adsorbent. Samples of an Algerian gas condensate, that contains mercury, were used, its density is  $0.7030 \text{ g.mL}^{-1}$ . The mercury concentration in the samples of gas condensate was among 23 and  $36.2 \text{ mg.L}^{-1}$ .

### 2.2. Batch Adsorption Tests

In the batch adsorption tests, named here as kinetic tests, different amounts of adsorbent were mixed into a series of gas condensate sample (100 mL). The so prepared mixtures are kept under agitation, using a flask shaker, at room temperature. Three different solid/liquid ratios were used, as shown on Table 1. Samples of the liquid were collected at each 1 hour time interval, until it had reached a nearly constant mercury concentration. Beside this, a first sample was collected after half an hour of the test beginning. The mass of adsorbed solute at the time  $i$  per unit mass of solid ( $q_i$ ) was calculated using the difference between the initial mercury concentration in the gas condensate ( $C_0$ ) and the remaining concentration at the same time ( $C_i$ ), through mass balance, Eq. (1),

$$q_i W = V(C_0 - C_i) \quad (1)$$

where  $W$  is the mass of adsorbent and  $V$  is the condensate volume, that is considered constant.

### 2.3. Determination of the Hg content

The total content of Hg in the condensate was determined using a mercury analyzer by adsorption in amalgam of gold with detection by flame photometry (NIC SP-3D from Nippon Instruments Corporation). The calibration curve was obtained using Hg standards (Merck N° 1.70226). The limit of detection of the technique is about 1 ppbw of Hg.

#### 2.4. Determination of diffusivity values

The homogeneous solid diffusion model (HSDM) was used for the estimation of the diffusivity. This is the simplest model to determine the diffusivity of solutes in solids, since it models the mass transfer in the solid as the diffusion in an amorphous and homogeneous sphere, without differentiating diffusion in the pores, diffusion in the surface (which happens after the adsorption), and diffusion within the solid material.

The equation that describes the diffusion in a homogeneous sphere, assuming constant diffusivity,  $D_s$ , in all the points of the particle, is:

$$\frac{\partial q}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial q}{\partial r} \right) \quad (2)$$

where  $q$  is the solute concentration in the solid, expressed in mass of solute per volume of the solid phase,  $t$  is the time, and  $r$  the radial position.

Crank, according to Cooney (1999), obtained an exact solution to this equation considering a single solute adsorption, where the sphere is initially free of solute and the solute concentration at the surface of the sphere is constant. The latter condition is often called "infinite bath case", since an infinite surrounding bath would provide a constant solute concentration at the solid surface, and also requires a negligible external resistance to mass transfer in the liquid film (i.e., a high mass transfer coefficient) near the solid surface. The solution obtained by Crank is given by:

$$\frac{q(r)}{q_s} = 1 + \frac{2R}{pr} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \operatorname{sen} \left( \frac{npr}{R} \right) \exp \left( \frac{-D_s n^2 p^2 t}{R^2} \right) \quad (3)$$

where  $R$  is the particle radius,  $t$  is the time,  $q_s$  is the mercury concentration in the solid at the interface, and  $q(r)$  represents the local value of the concentration in the solid phase.

However, it doesn't matter how  $q$  varies with the radial position  $r$ , but only the average concentration of solute in the solid at any particular time. The average value of  $q$  in a spherical particle, which is represented by  $\bar{q}$ , is given by:

$$\bar{q} = \frac{3}{R^3} \int_0^R q(r) r^2 dr \quad (4)$$

Substituting the solution for  $q(r)$ , (Eq. 3), into Eq. (4), Crank developed the following equation for the average concentration in the solid for any time:

$$\frac{\bar{q}}{q_{\infty}} = 1 - \frac{6}{p^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(\frac{-D_s n^2 p^2 t}{R^2}\right) \quad (5)$$

where  $D_s$  is the average or effective diffusivity ( $D_{ef}$ ) during the entire process, and  $q_{\infty}$  is the solute concentration in the solid corresponding to an infinite time.

**Diffusivity value from short time data.** At short times ( $\bar{q}/q_{\infty} < 0.3$ ) and considering the assumptions previously mentioned, the Eq. (5) can be written as:

$$\frac{\bar{q}}{q_{\infty}} = 6 \left(\frac{D_s t}{R^2}\right)^{1/2} [p^{-1/2} + L] \quad (6)$$

Although the kinetic tests should be done for a long time, to obtain the average solute concentration in the solid at an infinite time, only short-time values are necessary to plot the values of  $\bar{q}/q_{\infty}$  against to the square root of time,  $t^{1/2}$ . This plot should give a straight line of slope  $6(D_s/pR^2)^{1/2}$ , from which  $D_s$  can be estimated.

Since the assumption of a constant concentration of solute at the solid surface (in which the above equations are based) is reasonably good at short times, the approach of a constant  $D_s$  through the process of adsorption should represent the process adequately.

**Effective diffusivity value estimation.** It is known that  $D_s$  can present concentration dependence and thus it varies with the radial position and the time during the adsorption process. As observed by Cooney (1999), when this happens, the value of  $D_s$  determined at the short times is not more representative of the values of  $D_s$  in the later stages of the adsorption process.

Unfortunately, there is not an easy theoretical method to consider the effect of the concentration on  $D_s$ . In the case where it is suspected that  $D_s$  varies significantly with the time, the best method is to obtain an average or effective diffusivity,  $D_{ef}$ , determined by means of the Eq. (5), using data for the entire adsorption process.

It is important to remind that this equation is valid for negligible resistance in the liquid film and for large liquid volume. The analysis is much more complicated if the previous conditions are not satisfied. In this work, the Eq. (5) was implemented in the software Matlab to estimate the value of  $D_{ef}$ . It was observed that the obtained values of  $D_{ef}$  did not vary when the number of sum terms ( $n$ ) was greater than 20.

### 3. Results and discussion

The results of the accomplished kinetic tests and the diffusivity values estimated in this study are presented below.

#### 3.1. Kinetic Tests

The experimental conditions of the kinetic tests are presented in Table 1. In this table it is reported: the used solid/liquid ratios, given in gram of adsorbent per unit volume of gas condensate ( $\text{gS.mL}^{-1}$ ), the initial ( $C_0$ )

and final ( $C_f$ ) mercury concentrations in the gas condensate, the average temperature, the percentage of mercury reduction in the gas condensate and the time of test duration. In Table 1, it can be seen that the initial Hg concentrations are not constant, although the samples came from the same gas condensate.

**Table 1.** Kinetic test data

Solid/liquid ratio (gS.mL <sup>-1</sup> )	Hg concentration in the liquid ( $\mu\text{g Hg.L}^{-1}$ )		Reduction (%)	Average Temperature (°C)	Time of test duration (h)
	initial	final			
2.51	23.0	1.5	93.7	20	8
1.00	26.7	3.5	86.9	22	11
0.20	30.0	18.4	38.6	22	9
0.20	36.2	28.2	21.9	25	12

### 3.2. Diffusivity in the solid

To determine the diffusivity of the solute in the solid ( $D_s$ ) it is necessary to know the diameter of the adsorbent particle. In adsorption processes the Sauter mean is the most used mathematical expression to obtain the particle mean diameter. Sieve tests using 50 g of sample and the Tyler sieve series among 8 and 32 mesh were used to determine the mean diameter of the particle of the commercial adsorbent. The sieve tests were done in replicate and a Sauter mean diameter of 1.4 mm was obtained for the commercial adsorbent used in this study.

The Hg concentrations in the solid,  $q$ , in  $\mu\text{g}$  of Hg/mg of solid, for a time  $i$  were calculated from the mass balance, Eq. (1). The value  $q_\infty$  is the arithmetic mean value of the Hg concentrations in the liquid in the last points of the tests.

**Diffusivity in the solid determined at short times.** Table 2 shows the values of diffusivity in the solid estimated at short times using the Eq. (6). As an example, Figure 1 and Figure 2 show, respectively, the Hg concentration in the liquid as function of time and the  $\bar{q}/q_\infty$  values against the squared root of the time, both for the largest solid/liquid ratio (2.51 gS.mL<sup>-1</sup>).

**Table 2.** Mercury diffusivity in the commercial activated carbon

Solid/liquid ratio (gS.mL <sup>-1</sup> )	Initial Hg concentration in the gas condensate ( $\mu\text{g Hg.L}^{-1}$ )	Diffusivity $10^8 \cdot (\text{cm}^2 \cdot \text{s}^{-1})$	
		For short times Eq. (6)	Effective Eq. (5)**
2.51	23.0	5.3 (3 *)	11.5
1.00	26.7	2.7 (4 *)	4.0
0.20	30.0		
0.20	36.2	0.9 (10*)	2.5

\* Number of points used in slope calculation, \*\* For n = 20

In Figure 1 it can be verified that the rate of mercury removal is high at the beginning of the test and that it slowly decreases for contact times longer than about 2.5 hours. In Figure 2, it can be observed that after about 3 h (1.73 h<sup>1/2</sup>) a constant value of  $\bar{q}/q_\infty$  is reached. The diffusivity was determined using the three initial points and the Eq. (6). The obtained values of diffusivity are in the typical range for the diffusivity of organic solutes in

activated carbon, according data given in Cooney (1999). When comparing the short-time  $D_s$  values shown in Table 2, it can be said that they have the same magnitude order and that differences in the test conditions did not affect, significantly, the results.

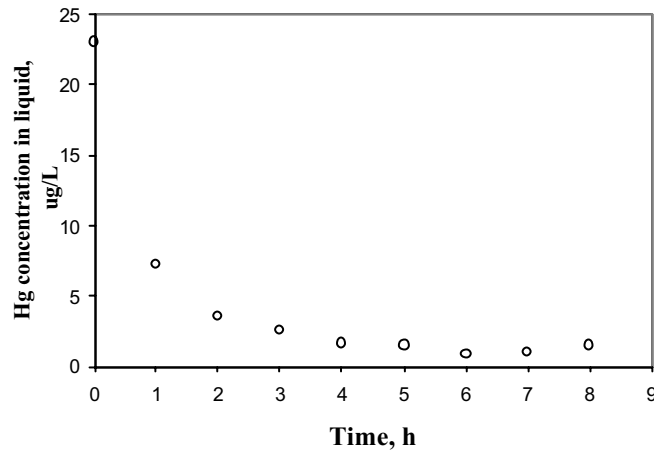


Fig. 1. Hg concentration in the liquid vs. time to 2.51 gS.mL<sup>-1</sup> ratio.

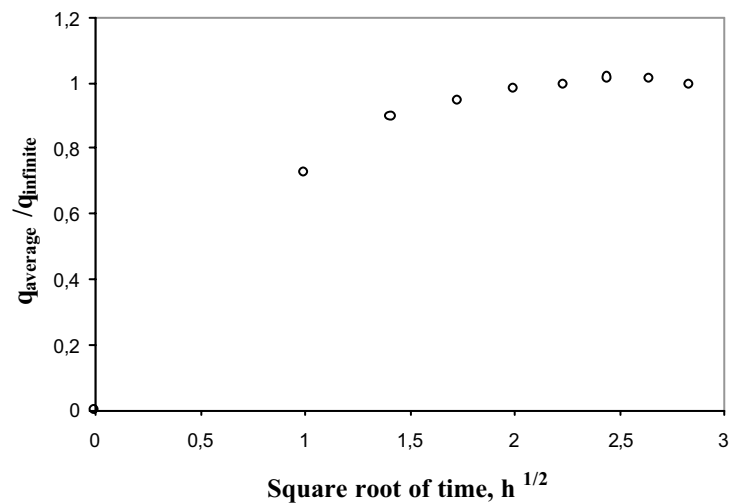


Fig. 2. Hg relative concentration in the solid vs. the square root of time to 2.51 gS.mL<sup>-1</sup> ratio.

**Effective diffusivity in the solid.** The values of effective diffusivity in the solid are also shown in Table 2. In this table it can be observed that for the 3 solid/liquid ratios used, the values of effective diffusivity are larger than the values of diffusivity at short times.

The experimental data obtained through the kinetic tests and the theoretical curves of  $\bar{q}/q_{\infty}$  against time calculated by Eq. (5) using both the diffusivity at short times and the effective diffusivity are presented in Figures 3 to 5. In these figures, it can be observed that the effective diffusivity better represents the uptake process than the diffusivity estimated at short times and, also, that the curves better fit the experimental data corresponding to the two larger solid/liquid ratios. However, it must be remarked that the number of experimental points at the short-time region is quite small. For the 0.20 gS.mL<sup>-1</sup> ratio (Figure 5), a larger dispersion of the experimental data was observed.

In Table 2, it can be observed that the effective diffusivity for the largest solid/liquid ratio is larger than that obtained for the other two solid/liquid ratios and that these diffusivity values are relatively close to each other. This indicates that diffusivity seems to be a function of the solute concentration in the solid.

In Figure 5, it is verified that for  $\bar{q}/q_{\infty} \leq 0.6$  and for times shorter than 5 hours the diffusivity estimated at short times better fits the experimental data than the effective diffusivity.

Finally, it is important to keep in mind that the used model considers the solid as an amorphous and homogeneous sphere and that there is only one solute to be adsorbed. On the other hand, Hg in hydrocarbons can exist in several forms, such as elemental, ionic, organic, which can be dissolved or suspended.

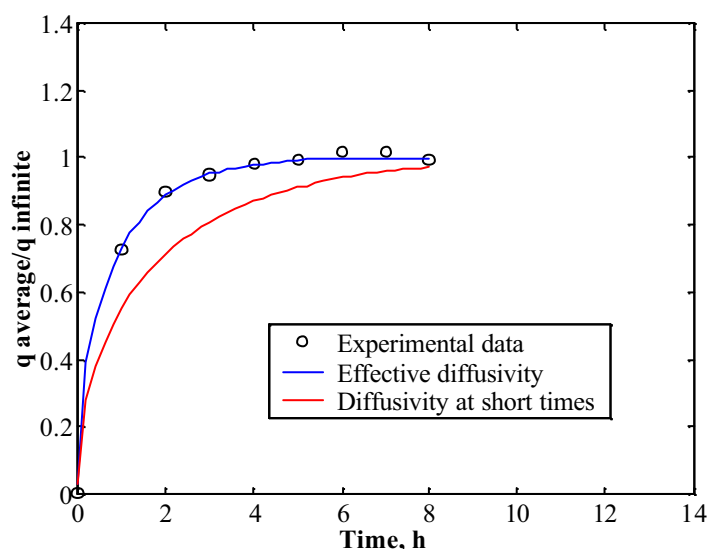


Fig. 3. Hg relative concentration in solid vs. time to 2.51 gS.mL<sup>-1</sup> ratio.

#### 4. Conclusions

For the used solid/liquid ratios the values of the diffusivity estimated at short times are smaller than the corresponding values for the effective diffusivity and they are in the values typical range of diffusivity for organic solutes in activated carbon. The effective diffusivity better represents the uptake process than the diffusivity estimated at short times, indicating the dependence of the diffusivity with the solute concentration in the solid.

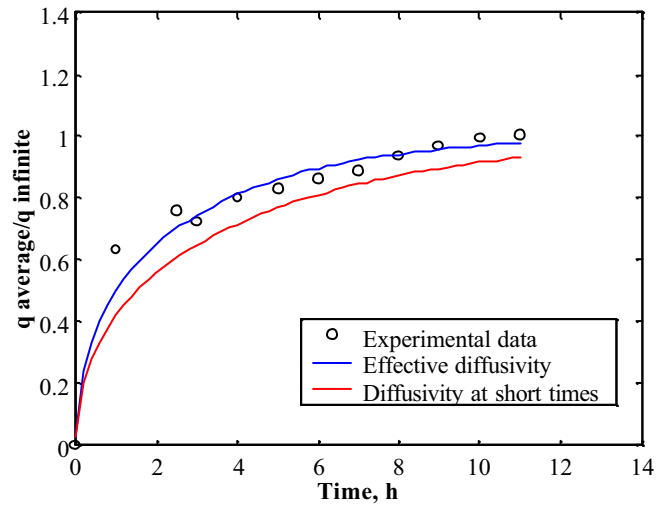


Fig. 4. Hg relative concentration in solid vs. time to 1.00 gS.mL<sup>-1</sup> ratio.

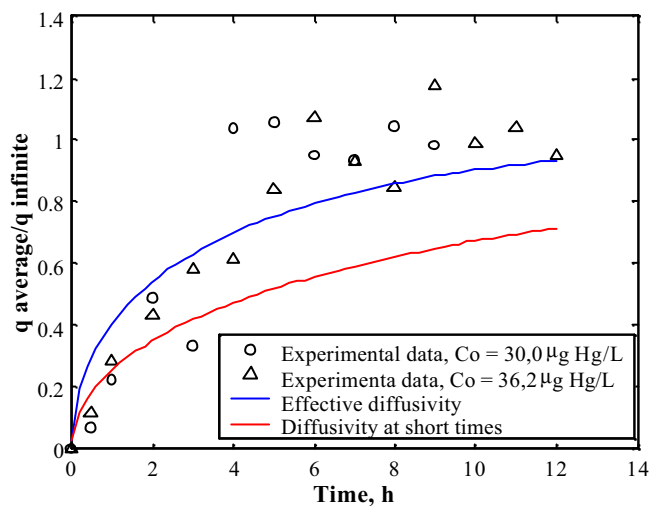


Fig 5. Hg relative concentration in solid vs. time to 0.20 gS.mL<sup>-1</sup> ratio.

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**2<sup>nd</sup> Mercosur Congress on Chemical Engineering**  
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