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Fundamental Mechanism of Combined Sorption of Highly and Weakly Soluble Volatile Organic Compounds into Aqueous Slurries of Activated Carbon

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Abstract. The sorption of two hydrophilic and two hydrophobic airborne VOC into aqueous slurries containing up to 50 kg activated carbon/m^3 was carried out in a cables scrubber to determine the effect of adsorbent particles. A reduction and an enhancement of the VOC uptake rate were observed respectively for the hydrophilic and the hydrophobic compounds. A model based on the penetration theory and taking account of the adsorption equilibrium and L-S mass transfer kinetics was developed to interpret the experimental findings.

Keywords: combined absorption and adsorption, VOC, activated carbon, aqueous slurries

1. Introduction

To control atmospheric emissions of volatile organic compounds (VOC), development of novel techniques or combination of well-known ones are new ways used to reach the required high abatement efficiencies.

The present study dealing with the scrubbing of VOC with an aqueous slurry of activated carbon (AC) is focused on a combination of two main techniques: absorption and adsorption. The advantages and drawbacks of this process were presented in a previous paper (Dubray and Vanderschuren, 2004).

Numerous studies relative to the effect of adsorbent particles in three phase absorption (Kars et al., 1979; Alper et al., 1980, 1981, 1986; Quicker et al., 1989; Tinge and Drinkenburg, 1992, 1995; Kim and Pingel, 1989) showed that the addition of fine activated carbon particles enhance substantially the liquid side mass transfer coefficient k_L whereas larger size particles have no significant or much less effect.

When the particle size is much smaller than the thickness of the liquid film close to the gas-liquid interface, diffusion and adsorption proceed in parallel which results in higher concentration gradient and enhanced mass transfer. This physical enhancement was attributed first by Kars et al. (1979) and later by Alper et al. (1980, 1981, 1986) to a "shuttle" unsteady-state mass transfer phenomenon. Particles present in the liquid bulk move from time to time into the liquid boundary layer close to the gas-liquid interface where they adsorb dissolved gas for a certain time and then return to the bulk of liquid in which desorption occurs until equilibrium is reached. A number of unsteady-state homogeneous and heterogeneous models were developed to describe this phenomenon (Holstvoogd, 1988; Holstvoogd and van Swaaij, 1990; Beenackers et al., 1993; Brilman et al., 2000).

Two other effects of the presence of adsorbing as well as non-adsorbing (inert) particles on k_L have been reported (Beenackers et al.,1993): 1. a reduction of this coefficient resulting from the decrease of the liquid volume available for diffusion of the dissolved species (Miyachi et al., 1981; Sada et al., 1984; Joosten et al., 1977); 2. an increase of k_L due to the enhancement of turbulence at the interface (Alper and Ozturk, 1986; Kluytmans et al., 2003) or an increase of the gas-liquid interfacial area.

The main objective of our research is to investigate the gas-liquid (G-L) and liquid-solid (L-S) mass transfer steps occurring in the system including the effect of

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AC particles in the liquid for highly and weakly soluble VOC.

2. Experimental Set-Up and Conditions

The combined sorption of 1–5 g/m^3 airborne VOC, two hydrophilic: isopropyl alcohol (IPA) and acetone, and two hydrophobic ones: 1–2 dichloroethane (DCE) and toluene, was carried out at room temperature in a cables scrubber operating semi-continuously with recycled aqueous suspensions containing up to 50 kg AC/m^3.

The cables scrubber, which was developed in our laboratory during the seventies (Lefebvre and AKZO, 1970, 1971a, 1971b), is a gas-liquid contacting unit with a packing made of parallel polypropylene cables of diameter 1.6 mm with a pitch of 8 mm. The absorbent flows down around the yarns in thin sheaths of high velocity and thickness equal to some tenth of mm. The laboratory scrubber used in the present work has a rectangular cross-section of 0.096 m × 0.150 m and 1 m of useful height. The experimental set-up was detailed in a previous paper (Dubray and Vanderschuren, 2004) focused on the two hydrophilic compounds. The gas velocity u_G was varied between 0.5 and 1.5 m/s and the liquid flow was fixed to the nominal value of ≈33 m^3/h m^2 ($u_L = 9.2\ 10^{-3}$ m/s).

3. VOC and Adsorbent Characteristics

Table 1 summarises the physical properties of the organic compounds used in this study, showing that their volatility and solubility in water vary in a large range.

The adsorbent is a chemically activated charcoal (Darco KB <100 mesh), provided in the wet state for purpose of easy addition to water. Its main characteristics are presented in Table 2. It was used without any pre-treatment.

Liquid-phase adsorption isotherms were determined by contacting volumes of solution with small amounts of AC in a batch of flasks continually stirred on an orbital shaker at 20°C until equilibrium. After filtration, analysis of the liquid was made by a purge and trap device coupled to a gas chromatograph. Isotherms were fitted empirically with Langmuir type equations:

$$q = aC_L \,/\, (1 + bC_L) \tag{1}$$

in which q (kg/kg AC) is the mass of adsorbed VOC and C_L (kg/m^3) the liquid concentration. For low C_L, they were approximated by straight lines of slope m (m^3/kg). Parameters of adsorption isotherms are reported in Table 1.

4. Liquid-solid Mass Transfer—Kinetics of Diffusion inside Particles

A determining step in the process is the mass transfer of dissolved VOC from the liquid to the adsorbent particles which includes external and internal diffusion. To study the adsorption kinetics, experiments were carried out with the same equipment as for isotherms, withdrawing at intervals of time one flask of liquid among a batch of ones filled initially with the same slurry. Two methods were used to determine the rate of liquid-solid mass transfer.

The first method combined a linear equation for liquid-solid mass transfer with the mass balances:

$$\frac{dq}{dt} = K_P\left(\frac{a\,C_L}{1 + b\,C_L} - q\right)a_P \tag{2}$$

$$\frac{dC_L}{dt} = -WK_P\left(\frac{a\,C_L}{1 + b\,C_L} - q\right)a_P \tag{3}$$

where K_P(m/s) is an overall L-S mass transfer coefficient, W (kg/m^3 water) the loading in AC of the slurry

Table 1. Physical properties of the VOC and parameters of adsorption isotherms.

VOC	Vapour pressure 20°C (kPa)	Henry's coefficient in water 20°C (m_L^3/m_G^3)	a (m^3/kg)	b (m^3/kg)	m (m^3/kg)
Isopropylalcohol	4.26	0.000208	0.0146	0.1674	0.0128
Acetone	24.60	0.000114	0.0404	0.4315	0.0306
1–2 Dichloroethane	8.26	0.00342	0.7114	8.9436	0.582
Toluene	2.91	0.15	10.18	131.8	8.313

Table 2. Characteristics of the activated carbon Darco KB.

Specific surface (m^2/g)	2062		
Pore volume (cm^3/g); micropores (cm^3/g)	1.86	0.89	
Functional surface groups, acid and basic (meq/g)	1.05	0.38	
Particle size $d_{v/v\%}$ (μm)	$d_{10} = 9$;	$d_{50} = 40$;	$d_{90} = 106$
Mean surface/volume particle size (μm)	$d_{3-2} = 16.2$		
Dry particle density, ρ_P (kg/m^3)	~600		
Water content (w/w%)	24.68		

and a_P (m^2/m^3 solid) the L-S specific interfacial area, defined with d_{3-2} the mean surface/volume diameter of particles:

$$a_P = 6/d_P = 6/d_{3-2} \tag{4}$$

These equations were solved with the known initial conditions ($C_L = C_{L0}$ and $q = 0$) by the Runge-Kutta method and the best values of K_P determined by minimization of the standard deviation between calculated and experimental curves of C_L/C_{L0} versus time. These values are given in Table 3.

Secondly, the equation of the homogeneous surface diffusion model HSDM (Do, 1998) was used with the liquid mass balance

$$D_S \left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r} \frac{\partial q}{\partial r} \right) = \frac{\partial q}{\partial t} \tag{5}$$

$$\frac{dC_L}{dt} = -W k_{LS} (C_L - C_{Li}) \frac{a_P}{\rho_P} \tag{6}$$

and the interface equations of flux continuity and phase equilibrium. This set of equations was solved by means of the finite difference Crank-Nicholson method. It was shown that the liquid film coefficient k_{LS} has no effect and that mass transfer is limited by internal diffusion, so that k_{LS} was estimated from a Sherwood number $k_{LS}\, d_{3-2}/D_L = 2$. Minimization of the standard deviation between experimental and computed C_L/C_{L0} led to the values of D_S and Biot number $= k_{LS} d_{3-2}/(D_S \rho_P m)$ reported in Table 3.

Table 3. Coefficients of liquid-solid mass transfer, 20°C, $Sh = 2$, $d_P = d_{3-2} = 16.2\ \mu$m.

VOC	K_P (10^{-9} m/s)	k_{LS} (10^{-4} m/s)	D_S ($10^{-14} m^2/s$)	Bi	m'/m
Acetone	3.94	1.35	0.738	16104	0.62
1-2 DCE	87.6	1.25	9.690	60	0.99
Toluene	7.49	1.05	0.870	39	0.10

5. Results of VOC Absorption into the Slurry and Effect of Non-Adsorbing Particles

Experimental results of the semi-continuous experiments of VOC sorption into the slurry provided asymptotic evolutions with time of the output concentration of VOC in the gas. They were treated to determine the G-L height of transfer unit H_{OG} of the scrubber according to the following assumptions (Dubray and Vanderschuren, 2004):

- a linear relationship in the initial times between the instantaneous VOC contents of the solid and liquid phases:

  $$q = m' C_L \tag{7}$$

  where m' may be more or less lower than the coefficient m due to the extent of the L-S mass transfer resistance.
- the liquid hold-up on the cables is negligible and the total liquid volume V_L in the scrubber is perfectly mixed.
- the slurry is replaced by an equivalent liquid volume $V_L(1+Wm')$ where Wm' is the actual or dynamic gain in uptake capacity of the liquid due to the presence of adsorbent.

As the liquid-solid mass transfer resistance is taken into account through the parameter Wm', the H_{OG} concerns the only gas-liquid transfer. The classical scrubber design theory provides well-known expressions of the HTU:

$$\begin{aligned} H_{OG} &= H_G + \frac{HG}{L(1 + W m')} H_L \\ H_G &= \frac{G}{k_G a S} \\ H_L &= \frac{L}{k_L a S} \end{aligned} \tag{8}$$

in which G and L are the gas and liquid flow rates (m^3/s) and H_G and H_L (m) the gas and liquid side HTU with

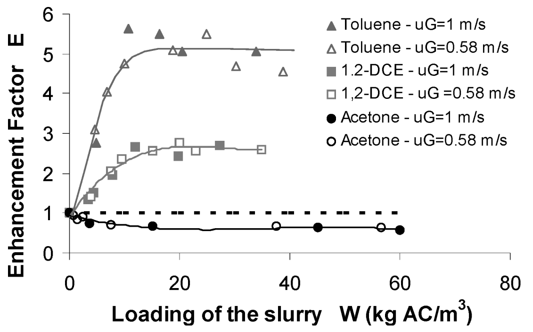

Figure 1. Enhancement factors.

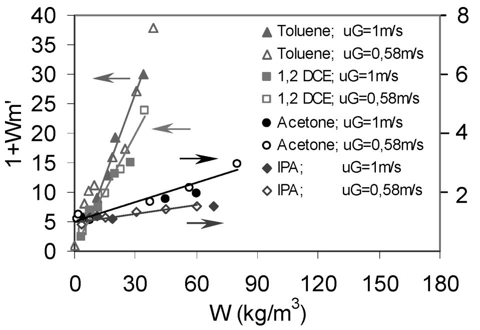

Figure 2. Dynamic gain of the slurry uptake capacity.

a, the gas-liquid interfacial area (m^2/m^3), and k_G, k_L (m/s) the gas and liquid film mass transfer coefficients. The values of H_G for the VOC were estimated from SO_2 absorption runs with sodium hydroxide solutions (Dubray and Vanderschuren, 2004). Overall gas-liquid $H_{OG,0}$ were obtained by absorption of VOC into water free of adsorbent, from which the $H_{L,0}$ and $k_{L,0}$ a for pure water were then drawn by means of Eq. (8). The same equations also allowed to compute the H_L and k_La for the runs carried out with the slurries of AC. Finally it was possible to calculate the enhancement factors of the liquid side mass transfer due to the adsorption process occurring in the liquid film:

$$E = k_L\, a / k_{L,0}\, a = H_{L,0}/H_L \tag{9}$$

The values of E are presented in Fig. 1 for acetone, 1,2-DCE and toluene, as functions of the loading in AC of the slurry W. It can be seen that the liquid phase transfer rate is reduced for acetone, whereas it is strongly enhanced for the two hydrophobic VOC, and the more for toluene, the more adsorbed compound. Furthermore, the general tendency of the curves is characteristic and similar for these two VOC. After an increase till about 15 kg AC/m^3, the enhancement factors reach quite constant values of ±2.5 and 5.0 for DCE and toluene respectively.

Also interesting is the Fig. 2 showing for all VOC the variation of the dynamic gain of uptake capacity of the slurry $1 + Wm'$ versus the loading W. Quasi-straight lines are obtained, the slopes of which allowing to estimate the values of m'. The ratio m'/m (see Table 3) characterises the degree of approach of L-S equilibrium in the whole slurry present in the experimental facility. It appears that equilibrium is reached for the 1,2-DCE and that m'/m increases with the internal diffusion coefficient D_S, taking also account, in case of almost equal D_S, of the much higher value of m and the much lower duration of runs for toluene (4 min) than for acetone (30 min).

Using aqueous slurries of fine silica particles of three different mean sizes ($d_{50} = 3$, 10 and 20 μm), some semi-continuous absorption runs of VOC were also carried out, as well as experiments of SO_2 absorption into sodium hydroxide solutions and CO_2 desorption from water (Dubray and Vanderschuren, 2004). These runs showed that the presence of inert particles in the liquid does not modify the $k_G a$ (and consequently the interfacial area 'a') whereas there is a strong decrease of the liquid film transfer coefficient with a rise of the volume fraction of solids in the slurry. For loadings higher than 15 kg/m^3, the mean reduction factor of k_L was about 1.75. This observation evidences that no increase of turbulence occurs at the interface. Moreover as 'a' remains constant, it can be concluded that the main influence of particles is not due to hydrodynamic effects in our kind of contactor.

It can be inferred, from these experiments, that a substantial hindering influence of the accumulation of particles in the liquid film close to the gas on the solute diffusion rate can also occur when adsorbing particles are added to the liquid. This is actually the case for the hydrophilic compounds for which the effect of adsorption is negligible (see Fig. 1). On the contrary, for the hydrophobic VOC, the favourable effect of adsorption greatly overcompensates the decrease of liquid diffusivity which leads to net enhancement factors much higher than 1.

6. Modelling of Simultaneous Diffusion and Adsorption of Dissolved VOC

To interpret all experimental findings, a model was developed, based on the fundamental mass transfer

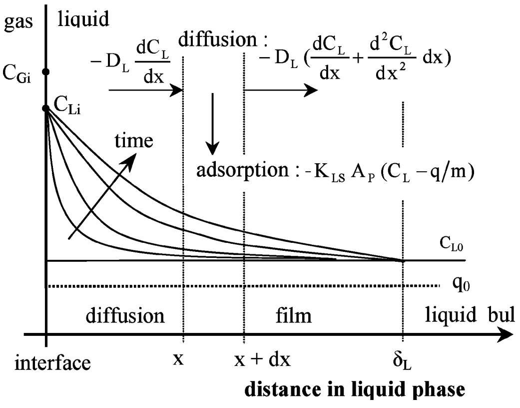

Figure 3. Sketch of diffusion with adsorption.

mechanism involved in the slurry, that is the shuttle movement of elements coming at the G-L interface where they undergo an unsteady-state diffusion process. Actually, the classical penetration model used in absorption was completed to take account of the presence of the adsorbent in the liquid. Equations describing the phenomenon are (10): diffusion of absorbed species in liquid elements accompanied by adsorption on AC particles expressed by a linear relation (see Fig. 3) and (11): liquid-solid mass transfer:

$$\frac{\partial C_L}{\partial t} = D_L \frac{\partial^2 C_L}{\partial x^2} - K_{LS} A_P \left(C_L - \frac{q}{m} \right) \quad (10)$$

$$\frac{\partial q}{\partial t} = K_P \, a_P \, (m \, C_L - q) \quad (11)$$

in which A_P (m^2/m^3) is the specific interfacial area of particles by m^3 of liquid and K_{LS} (m/s) an overall liquid-solid transfer coefficient, based on the liquid side:

$$A_P = W a_P / \rho_P \qquad K_{LS} = K_P \, \rho_P \, m \quad (12)$$

The assumed boundary conditions are G-L-S equilibrium at the interface ($x = 0$) at every time ($t \geq 0$), L-S equilibrium everywhere in the slurry ($x > 0$) at the initial time and constant liquid and solid concentrations at $x = \delta_L$, the thickness of the diffusion film. The set of equations was solved numerically by the Crank-Nicholson method to get the evolution with time of the concentration profiles which allow to compute the mean flux at the interface during the contact time τ and the enhancement factor E defined by Eq. (9) as:

$$E = \left(\frac{1}{\tau} \int_0^{\tau} -D_L \left. \frac{\partial C_L}{\partial x} \right|_{x=0} dt \right) \Big/ \left(2 \sqrt{\frac{D_L}{\pi \tau}} \, (C_{Li} - C_{L0}) \right) \quad (13)$$

Using the experimental values of the mean adsorption equilibrium coefficient m and the liquid-solid transfer coefficient $K_P a_P$ (Tables 1 and 3) to run the model with an homogeneous distribution of particles in the slurry resulted in values of E close to unity. To improve the model, the following considerations were taken into account.

As particles of low wettability present in the liquid have a large tendency to concentrate at the G-L interface, mainly because of superficial tension forces, we assumed that all AC particles accumulate at the interface in a liquid layer of thickness equal to one particle diameter d_{3-2} (Dubray, 2004). Knowing the velocity profile of the liquid flow down the cables (Lefebvre et al., 1979) for the used liquid rate, the continuity equation allowed to calculate the loading in particles in the superficial layer W_S and the volume fraction of liquid ε_S. To consider the reduction of liquid phase mass transfer due to particles, an effective diffusion coefficient including a tortuosity factor t_{OR} was defined, and a good mean value of $t_{\mathrm{OR}} = 1.6$ was found by fitting the observed reduction by 1.75 of the k_L obtained in CO_2 desorption runs with inert silica particles. Including above features in the model provided a good fit for acetone (see Fig. 4), showing that, for this weakly adsorbed species, the main effect of particles is to create a barrier to diffusion in the liquid phase. On the

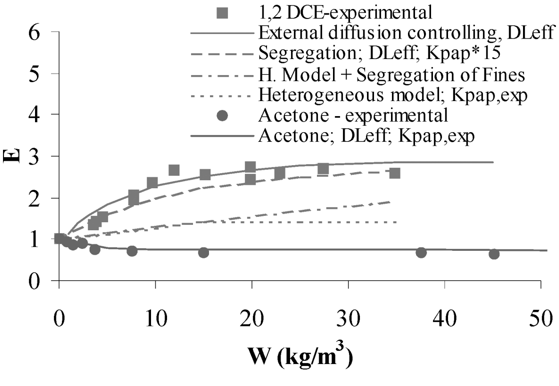

Figure 4. Simulation results given by the model.

contrary, for 1,2-DCE, the factor E remained largely underestimated and further improvements concerning the L-S mass transfer had to be brought.

First, as particles which are likely to be caught by the G-L interface are the finest ones, we assumed that only those of size less than d_{3-2} are picked up in the superficial layer. This segregation of fines results in an increase of the $K_P a_P$ which is proportional to d_P^{-2} (at constant D_S, $K_P \div d_P^{-1}$ and $a_P = 6/d_P$). An effective $K_P a_P$ was computed from the particle size distribution of AC particles, providing a 7 times increase of $K_P a_P$ while reducing W_S by 5. Figure 4 shows that the effect on the factor E remained weak and the coefficient $K_P a_{P|\text{eff}}$ had still to be raised, by a factor somewhat larger than 15. This might seem to be quite arbitrary so that investigation was continued.

It appeared finally that a very good fit of the experimental results with the simulations was achieved if one assumes that the liquid-solid mass transfer is controlled only by the liquid film diffusion outside particles, while keeping the segregation of fines into the superficial layer and the reduced diffusivity (Fig. 4). In this case $K_P = k_{LS}/m\ \rho_P$, the mean k_{LS} being calculated with $Sh = 2$ and the size distribution of segregated particles. Due to the very short contact times (0 to 0.3 s) of particles at the interface where they undergo a step of transfer potential, the internal diffusion rate can reach very high values. Actually, the flux is then limited by the external transfer and the mean experimental $K_P a_P$ determined by much longer duration runs on the orbital table are obviously not valid.

Unfortunately, the model provided $E_{\max} = 3$ for toluene which did not fit the high experimental value of 5. This is likely caused by highly inaccurate absorption measurements due to the very low solubility of this species.

7. Conclusion

Sorption runs of airborne hydrophilic and hydrophobic VOC into aqueous slurries of activated carbon resulted in reduction and enhancement factors of mass transfer due to the presence of adsorbent particles. A comprehensive penetration model was developed to simulate the non-stationary diffusion–adsorption phenomenon occurring in slurry elements which come contact the gas. It confirmed that the finest AC particles accumulate in a thin layer close to the interface and allowed to interpret the influences on the enhancement factor of the adsorption capacity, the loading in adsorbent of the slurry, the L-S mass transfer kinetics and the reduction of diffusivity in the liquid.

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