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Adsorption of Halogenated Hydrocarbons from Aqueous Solutions by Wetted and Nonwetted Hydrophobic and Hydrophilic Sorbents: Equilibria

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Single-solute adsorption equilibria of 1,1,1-trichloroethane, 1,1,2-trichloroethane, trichloroethene, *trans*-1,2-dichloroethene, chloroform, 2,4-dichorophenol, and dichloromethane dissolved in water have been measured, using both wetted and nonwetted hydrophobic Amberlite XAD-4 resin at 20 °C. The results could be described by means of Freundlich isotherms indicating the heterogeneity of the Amberlite XAD-4 surface. Wetted and nonwetted Amberlite XAD-4 showed identical adsorption capacities. The influence of the ionic strength on the adsorption capacity of Amberlite XAD-4 for 1,1,1-trichloroethane has been measured by adding KCl to the aqueous solution. The apparent adsorption capacity was found to increase with salt concentration due to the salting-out effect. Adsorption equilibria of dichloromethane, which is generally regarded as a key component with regard to water treatment demands, have also been measured using several other synthetic resins, as well as activated carbon. The order of increasing adsorption capacity was found to be Amberlite XAD-7 < Amberlite XAD-4 ≈ Dowex XUS 43493.00 < Norit ROW 0.8 SUPRA < Ambersorb XE-572 < Ambersorb XE-563.

Introduction

Contamination of surface water and groundwater with halogenated hydrocarbons is one of the many environmental problems mankind faces today. Stricter legislation has resulted in continuously decreasing emissions, yet a considerable amount is still being emitted to the environment. A large number of water treatment methodologies is available, of which adsorption using activated carbon is one of the most frequently applied techniques for the removal of trace pollutants. The main disadvantage of activated carbon is the inability to desorb adsorbed components completely (Kennedy, 1973a; Cornel, 1986).

In the early 60s synthetic sorbents became available that can easily be regenerated by acids, bases, or organic solvents but also by hot gases or steam, which makes on-site regeneration a technically and economically attractive option. Besides regenerability, synthetic sorbents may have a number of other advantages, such as selectivity, fast intraparticle mass transport, low regeneration costs, and physical and chemical stability.

To design a wastewater treatment system on the basis of adsorption techniques, detailed information is needed about the adsorption equilibrium. In this paper we will present the adsorption isotherms of several halogenated hydrocarbons onto wetted and nonwetted Amberlite XAD-4 resin. These hydrocarbons are dissolved in water at 20 °C. Furthermore, the influence of ionic strength on the adsorption equilibrium of 1,1,1-trichloroethane onto nonwetted Amberlite XAD-4 has been determined. Finally, the adsorption isotherms of dichloromethane onto several synthetic sorbents, as well as activated carbon, will be treated.

Theory

Synthetic polymer sorbents are extremely heterogeneous because of chemical impurities that are incorporated in their matrixes during polymerization and because of physical inhomogeneities such as cavities and bulges in their pores. As a consequence, for nearly all synthetic polymer sorbents the enthalpy of adsorption decreases logarithmically with surface coverage. Halsey (1952) has shown that adsorption on such sorbents can be well described by the Freundlich isotherm, although its thermodynamic consistency at zero coverage remains questionable, as the enthalpy of adsorption takes an infinite value. The Freundlich isotherm is expressed by

$$q = K_{\mathrm{F}}^{\mathrm{l}} c_l^{1/n_{\mathrm{F}}^{\mathrm{l}}} \text{ (liquids)} \tag{1a}$$

or

$$q = K_{\mathrm{F}}^{\mathrm{g}} p^{1/n_{\mathrm{F}}^{\mathrm{g}}} \text{ (gases)} \tag{1b}$$

where q is the sorbent loading of dry resin, c_{l} is the solute concentration in the liquid phase, p is the partial pressure of the solute, and K_{F} and n_{F} are constants which depend on temperature, type of sorbent, and type of solute.

A major drawback of the Freundlich isotherm is the impossibility to determine the values of the applied constants a priori from adsorbate properties, solution conditions, and the nature of the adsorbent. Several attempts have been made to overcome this problem. Gibbs (1961) applied a thermodynamic approach and assumed that the interface between two phases can be regarded as a separate surface phase. By formulating the conditions for thermodynamic equilibrium between the three phases, the Gibbs relative adsorption isotherm is obtained. Later, this approach was extended by Rixey (1987), who used a surface phase model to describe the adsorption of polar organic solutes on wetted and nonwetted sorbents and was able to predict the relative difference in adsorption capacity between these sorbents. However, it remained impossible to predict the actual value of the adsorption capacity due to

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Table 1. Boiling Temperature t_{boil}, Molar Mass M, Activity Coefficient at Infinite Dilution γ^{∞}, and Other Properties of Applied Hydrocarbons at 20 °C

name	purity/mass %	t_{boil}[c]/°C	M[c]/kg mol^{-1}	solubility in water/mass %	density[c]/kg m^{-3}	γ^{∞} [d]
1,1,1-trichloroethane	>99	74	0.1335	0.095[f]	1339	5595
1,1,2-trichloroethane	>98	114	0.1335	0.45[f]	1432	1520
t-1,2-dichloroethene	>98	47.5	0.0970	0.630[f,h]	1257	1201
trichloroethene	>99.5	87	0.1315	0.107[f]	1464	5166
chloroform	>99	61	0.1195	0.825[a]	1480	802
dichloromethane	>99.5	39.8	0.0849	1.722[a]	1316	268
2,4-dichlorophenol	>99	210	0.1630	0.45[b]	1388[g]	2012[e]

[a] Horváth (1995). [b] Horváth (1985). [c] Weast (1983). [d] Averaged data of Gmehling (1994). [e] At saturation, as calculated from solubility. [f] Grayson (1979). [g] Kroschwitz (1993). [h] At 25 °C.

Table 2. Matrix Density ρ, Particle Porosity ϵ_p, and Other Physical Properties of Sorbents Used

name	ρ/kg m^{-3}	ϵ_p	av pore size/Å	BET surface area/m^2 g^{-1}	hydrophobic
Amberlite XAD-4[a]	1080	0.51	51	775	yes
Amberlite XAD-7[a]	1251	0.57	50	450	no
Dowex XUS-43493.00[b]	1160	0.54	35	1125	no
Ambersorb XE-563[a]	1620	0.49	38	550	yes[d]/no[e]
Ambersorb XE-572[a]	1938	0.62	30	1100	no
Norit ROW 0.8 SUPRA[c]	2170	0.68	19	1125	no

[a] Manufactured by Rohm and Haas. [b] Manufactured by DOW Chemical. [c] Manufactured by Norit. [d] According to manufacturer. [e] 90% of sorbent wets within 10 min, whereas the remaining 10% is wetted after 2 h.

the introduction of unknown interfacial tensions and surface-phase activity coefficients. Belfort et al. (1983) used the solvophobic theory (see also Horváth et al., 1976) to predict the adsorption capacity for different organic solutes. Although this theory is quite promising from a fundamental point of view, its main disadvantage is the introduction of a large number of energy contributions which still are difficult to calculate a priori. For this reason the solvophobic theory and surface-phase models are not suitable in most practical cases.

Influence of Salt Additions. At increasing ionic strength of an aqueous solution, the adsorption capacity for hydrophobic solutes increases through the so-called salting-out effect (Kennedy, 1973b). This effect also becomes manifest through the distribution coefficient m_s^{corr}, which is defined as the ratio of the solute concentrations in the gas and liquid phases. This coefficient will rise with increasing salt concentration. It can be calculated as a function of ionic strength using (Gosset, 1987)

$$m_s^{corr} = \frac{c_g}{c_l} = m_s^{\circ} 10^{sI} \tag{2}$$

where m_s° is the distribution coefficient for salt-free water, s is the salting-out coefficient, and I is the ionic strength, which is defined as

$$I = \frac{1}{2} \sum z_i^{\,2} c_i \tag{3}$$

where z_i represents the ionic charge of ion i. In the case of a nonwetted adsorbent, pores are filled with gas rather than liquid. In that case adsorption takes place at the resin–vapor interface (i.e. pore wall) and the actual adsorption isotherm can be expressed by

$$q = K_F^g {c_g}^{1/n_F^g} \tag{4}$$

where c_g represents the concentration of the gaseous solute in the pores of the adsorbent. Since salt ions are unable to evaporate into the gas phase, it is most likely that the Freundlich constants of eq 4 are unaffected by the presence of salt ions in the water phase. However, when eq 1a is used to predict sorbent loading, the Freundlich constant K_F^l will depend on the ionic strength, as can be shown by combining eqs 1a, 2, and 4:

$$K_F^l = (10^{sI/n_F}) K_F^{l,I=0} \tag{5}$$

where $K_F^{l,I=0}$ is the Freundlich constant when no ions are present in solution. When the salting-out coefficient is positive, the apparent adsorption capacity increases with ionic strength due to an increased solute concentration in the gas phase.

Experimental Section

Materials. Relevant physical properties of all applied hydrocarbons (obtained from Merck) are presented in Table 1. Table 2 shows relevant physical properties of the investigated sorbents. If a sorbent was not wetted after 1 day of contact with distilled water, it was referred to as hydrophobic. All synthetic sorbents had a spherical shape, whereas the activated carbon particles had a cylindrical shape. Amberlite XAD-4 is a macroreticular polystyrene–divinylbenzene copolymer. Ambersorb XE-563 and XE-572 also are macroreticular polystyrene–divinylbenze copolymers but have been sulfonated and pyrolyzed afterward. Amberlite XAD-7 consists of a carboxilic ester. The Amberlite and Ambersorb sorbents are composed of a large number of nonporous microspheres with diameters ranging from 30 Å to 1000 Å (Gustafson et al, 1968). Dowex XUS-43493.00 is a highly cross-linked styrenic polymer.

Sorbent Preparation. A review on cleaning methods of XAD resins was given by Daignault et al. (1988). Methods for cleaning the resin range from simple rinsing to exhaustive Soxhlet extraction, depending on the field of application. Resins used for analysis purposes should be extremely clean, whereas this is not the case when resins are used for wastewater treatment.

Prior to use, the synthetic resins were thoroughly washed for 24 h with methanol (Merck, purity > 99.8 mass %), using 20 mL per gram of sorbent. After most of the methanol had been removed, the resins were washed for

24 h with distilled water using 200 mL per gram of sorbent. Subsequently, the resins were dried at room temperature for 2 days in order to remove most of the water. Next, the sorbents were dried in a vacuum oven for 24 h at 105 °C, and finally, the resins were stored in an airtight container. A comparable procedure was applied by Rixey (1987). The activated carbon has been prepared using the same procedure without applying the washing step using methanol.

The hydrophilic sorbents were readily wetted when brought into contact with distilled water. When wetted hydrophobic sorbents were to be applied, the following procedure for wetting was applied. First, the hydrophobic particles were thoroughly rinsed with methanol using 20 mL per gram of sorbent. After a while no more air bubbles emerged, indicating that all pores were filled with methanol. Subsequently, the methanol was displaced by distilled water by washing the sorbent for 24 h with 200 mL of distilled water per gram of resin. The wetted resins were stored in an airtight container which was saturated with water vapor.

Adsorption Experiments. Adsorption experiments were conducted by using small vials with a volume of 3.5 mL, which were provided with a screw top and a septum. The vials were filled with different amounts of sorbent, varying from 0.01 to 0.15 g, while the remaining volume was filled with a known amount of distilled water. Next, a known amount of solute was injected through the septum using a 10 μL syringe. Subsequently, the vials were rotated in a thermostat bath for at least 24 h to reach equilibrium. Measurements after 24 and 48 h of equilibration gave equal results, and it was concluded that 24 h was long enough for the sorbent to reach equilibrium. The solute uptake was determined from the depletion of solute in solution, which was measured using a Varian Model 3600 gas chromatograph equipped with a DB-5 column (length = 30 m, i.d. = 0.53 mm, film = 1.5 μm) and an electrolytic conductivity detector (ELCD, 1000 HALL Detector). The adsorbed amount of component b from a binary mixture of components a and b was calculated from (Parfitt, 1983)

$$n^\circ \frac{\Delta x_\mathrm{b}}{m} = q_\mathrm{b}(1 - x_\mathrm{b}) - q_\mathrm{a} x_\mathrm{b} \qquad (6)$$

where n° is the total number of moles in solution, m is the sorbent mass, x_b is the mole fraction of component b, and q_a and q_b are the sorbent loadings of components a and b, respectively. At small mole fractions of b, eq 6 reduces to,

$$V\frac{\Delta c_\mathrm{b}}{m} = q_\mathrm{b} \qquad (7)$$

with V being the total liquid volume. The influence of ionic strength was demonstrated by measuring the adsorption capacity of nonwetted Amberlite XAD-4 for 1,1,1-trichloroethane at various KCl concentrations. Five vials were filled with 55 mg of resin whereas the remaining volume was filled with distilled water containing different salt amounts. Next, 10 μL of 1,1,1-trichloroethane was injected through the septum. Finally, the sorbent loading at equilibrium was determined by the method described above.

Results and Discussion

First adsorption onto wetted and nonwetted Amberlite XAD-4 will be treated. Next, the influence of salt addition on the adsorption of 1,1,1-trichloroethane by nonwetted Amberlite XAD-4 will be dealt with. Finally, the adsorption of dichloromethane by several other sorbents will be treated.

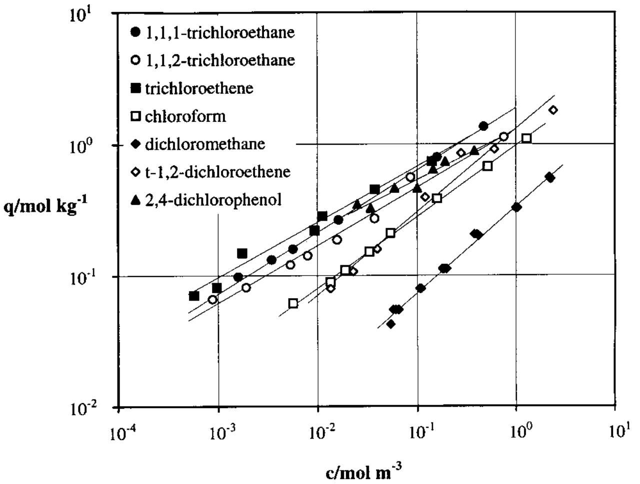

Figure 1. Adsorption isotherms of halogenated hydrocarbons on wetted Amberlite XAD-4 at 20 °C; capacity q against solute concentration c.

Adsorption of Halogenated Hydrocarbons onto Wetted Amberlite XAD-4. Because of its hydrophobic character, Amberlite XAD-4 is not wetted spontaneously by water. In most studies hydrophobic sorbents are wetted prior to adsorption using a wetting procedure (Gustafson et al, 1968; Paleos, 1969; van Vliet and Weber, 1981; Cornel and Sontheimer, 1985). Therefore, we also applied wetted sorbent material. Figure 1 shows the measured adsorption isotherms of 1,1,1-trichloroethane, 1,1,2-trichloroethane, *trans*-1,2-dichloroethene, trichloroethene, chloroform, dichloromethane, and 2,4-dichorophenol on wetted Amberlite XAD-4 at 20 °C. The sorbent loading is given per kilogram of dry resin.

The Freundlich isotherm (eq 1a) fits the experimental data very well and is represented as solid lines in Figure 1. The Freundlich constants at 20 °C are shown in Table 3.

Apparently, the adsorption capacity at a certain concentration increases with increasing activity coefficient (γ^∞ in Table 1), which suggests that the latter might be a determining factor with regard to adsorption capacity. In Figure 2 the adsorption capacity is plotted versus aqueous solute activity a, which is calculated according to

$$a = \gamma^\infty x = \gamma^\infty c_\mathrm{l}\frac{M_\mathrm{l}}{\rho_\mathrm{l}} \qquad (8)$$

With x the mole fraction of the solute, M_l the molar mass of the liquid, and ρ_l the density of the liquid. It is assumed that the activity coefficient at infinite dilution is valid for the whole concentration range that has been applied. The activity coefficient of 2,4-dichlorophenol has been calculated from its saturation mole fraction in water x^s, using $\gamma^\mathrm{s} = 1/x^\mathrm{s}$.

Figure 2 shows that the adsorption mechanism and also enthalpy are comparable for the hydrocarbons under consideration. The adsorption isotherms of Figure 2 lie much closer to each other than in Figure 1, possibly because a better measure for the driving force for adsorption was applied. Small differences between the adsorption isotherms can be observed which are probably caused by differences in the adsorption mechanism, but also by experimental errors and the use of inaccurate values for the activity coefficient.

Adsorption of Several Halogenated Hydrocarbons onto Nonwetted Amberlite XAD-4. When using a non-

Table 3. Freundlich Constants for Wetted and Nonwetted Amberlite XAD-4 at 20 °C

	wetted		nonwetted	
solute	$K_{\mathrm{F}}^{\mathrm{l}}$	$1/n_{\mathrm{F}}^{\mathrm{l}}$	$K_{\mathrm{F}}^{\mathrm{l}}$	$1/n_{\mathrm{F}}^{\mathrm{l}}$
1,1,1-trichloroethane	1.87 ± 0.16[a]	0.47 ± 0.02	1.66 ± 0.37	0.43 ± 0.05
1,1,2-trichloroethane	1.29 ± 0.33	0.44 ± 0.06	1.14 ± 0.11	0.48 ± 0.03
trichloroethene	1.77 ± 0.68	0.42 ± 0.07	1.75 ± 0.29	0.44 ± 0.04
chloroform	0.97 ± 0.08	0.54 ± 0.02	0.88 ± 0.15	0.44 ± 0.05
dichloromethane	0.33 ± 0.02	0.66 ± 0.03	0.28 ± 0.02	0.69 ± 0.04
trans-1,2-dichloroethene	1.30 ± 0.43	0.63 ± 0.12	1.72 ± 0.13	0.75 ± 0.03
2,4-dichlorophenol	1.28 ± 0.35	0.38 ± 0.11	1.19 ± 0.28	0.52 ± 0.12

[a] 95% confidence limit.

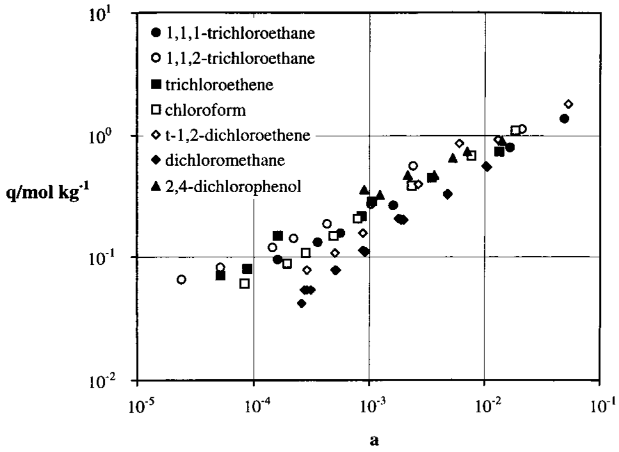

Figure 2. Adsorption isotherms of halogenated hydrocarbons on wetted Amberlite XAD-4 at 20 °C; capacity *q* against solute activity *a*.

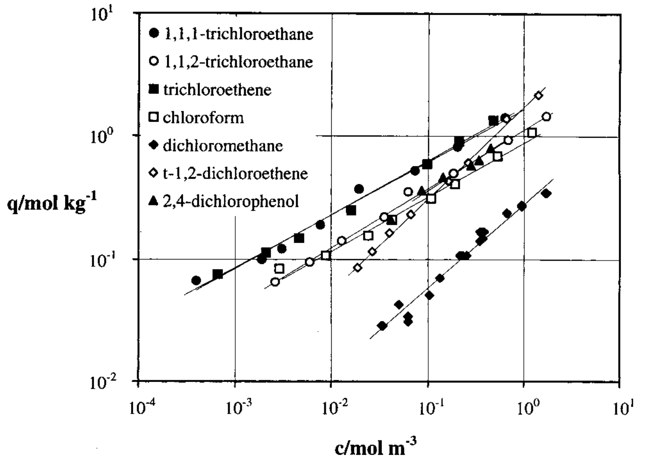

Figure 3. Adsorption isotherms of halogenated hydrocarbons on nonwetted Amberlite XAD-4 at 20 °C; capacity *q* against solute concentration *c*.

wetted sorbent, adsorption takes place at the resin–vapor interface which is located at the pore walls. First the solute has to evaporate into the gas phase inside the pores of the sorbent before it can be adsorbed at the internal resin surface. Figure 3 shows the adsorption isotherms that were measured with nonwetted Amberlite XAD-4 at 20 °C.

The observed adsorption capacities are considerable and of the same magnitude as those measured for wetted XAD-4. Again the isotherms can be satisfactorily fitted using the Freundlich equation, as represented by the solid lines in Figure 3. The Freundlich constants for nonwetted XAD-4 are shown in Table 3.

Wetted versus Nonwetted: A Comparison. In Figure 4 the adsorption capacities of wetted and nonwetted XAD-4 are compared for each hydrocarbon. No large differences are observed for the relatively apolar hydrocarbons applied in this study. This result differs from the results obtained by Rixey (1987), who observed, in the case of small carboxylic acids and alcohols, that the adsorption capacity of nonwetted Amberlite XAD-4 was no more than 15% of the capacity of wetted XAD-4. Apparently, in the case of more polar hydrocarbons, the presence of water inside the pores of a resin results in a higher adsorption capacity.

We believe that the explanation for the observed difference is to be found in the chemical constitution of acids and alcohols on one hand and of hydrophobic halogenated hydrocarbons on the other. The molecules of carboxylic acids and alcohols both contain a hydrophobic and a hydrophilic part. In the case of a wetted resin, the hydrophobic carbon chain is adsorbed at the resin surface whereas the hydrophilic part of the molecule is directed toward the water phase where additional stabilization at the resin–water interface is achieved by hydrogen bonds. This is illustrated in Figure 5. When the water phase is absent, such stabilization does not occur, which results in a lower adsorption capacity. With the exception of 2,4-dichlorophenol, the hydrophobic halogenated hydrocarbons used in this study do not contain a hydrophilic part in their molecules and the presence of water in the pores of the Amberlite XAD-4 resin hardly influences adsorption capacity. As to be expected, the largest difference is observed with 2,4-dichlorophenol.

Influence of Salt Additions. The results of the salting-out experiments are shown in Table 4. The values of $K_{\mathrm{F}}^{\mathrm{l}}$ were calculated using eq 1a while assuming that the Freundlich constant $1/n_{\mathrm{F}}^{\mathrm{l}}$ (0.43) does not vary with the ionic strength. As is to be expected in the case of a positive salting-out coefficient (a value of 0.193 was measured by Gosset (1987) for 1,1,1-trichloroethane), the Freundlich constant $K_{\mathrm{F}}^{\mathrm{l}}$ increases with KCl concentration.

In Figure 6 the experimentally obtained Freundlich constants are plotted against ionic strength, which in the case of a monovalent salt like KCl is equal to the concentration.

Equation 5 fits the experimentally obtained Freundlich constants very well when using a salting-out coefficient of 0.305 L/mol, which is higher than the value of 0.193 that Gosset (1987) measured for concentrations smaller than 1 M.

Adsorption of Dichloromethane Using Several Different Sorbents. Dichloromethane is known as a component which is difficult to remove from wastewaters by adsorption. See also Figures 1 and 3 of this paper. The adsorption capacity of several different sorbents for dichloromethane has therefore been investigated. Figure 7 shows the adsorption isotherms of dichloromethane onto the sorbents Amberlite XAD-4, Amberlite XAD-7, Ambersorb XE-563, Ambersorb XE-572, Dowex XUS-43493.00, and Norit ROW 0.8 SUPRA, which were all wetted by water.

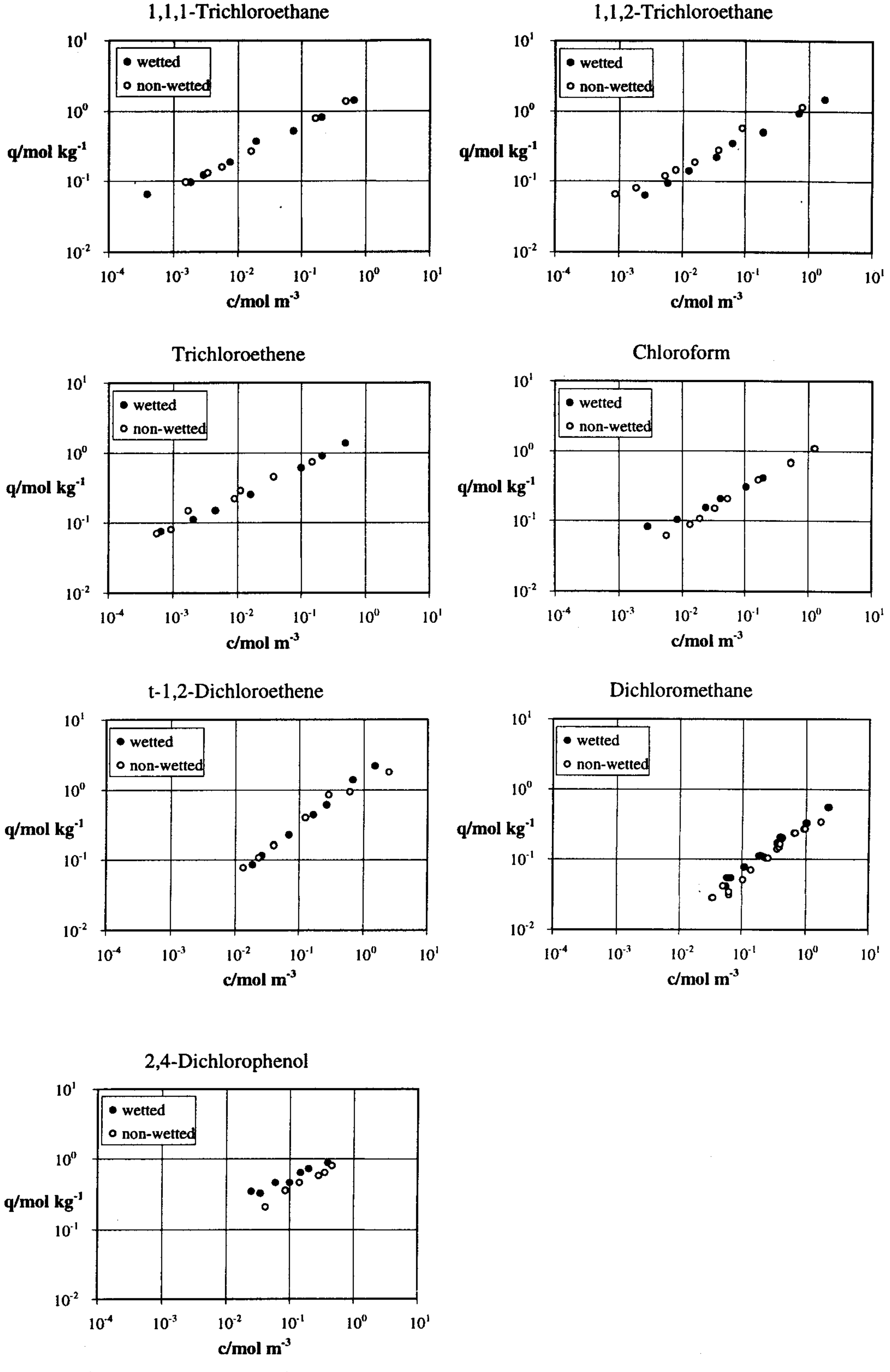

Figure 4. Comparison of adsorption isotherms for wetted and nonwetted Amberlite XAD-4 at 20 °C.

The derived Freundlich constants are summarized in Table 5. Both Ambersorb sorbents show a high adsorption capacity for dichloromethane. However, though the internal surface area of Ambersorb XE-572 is twice as large as the surface area of Ambersorb XE-563 (See Table 2), its adsorption capacity is lower, especially at lower concentrations. This is also illustrated in Figure 8, in which the loading per unit of surface area *q′* is plotted against the solute concentration.

Apparently the hydrophobic nature of Ambersorb XE-563 has a positive effect on adsorption capacity (See Table 2). Amberlite XAD-4, which is the most hydrophobic sorbent under investigation, has a much lower adsorption capacity than Ambersorb XE-563, which shows that hydrophobicity is not the only factor determining adsorption capacity. As Ambersorb XE-563 contains smaller pores than Amberlite XAD-4, it seems plausible that the size of the pores may be important with respect to the adsorption

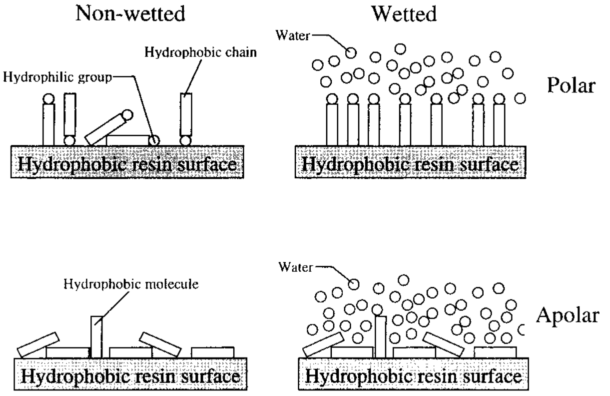

Figure 5. Adsorption behavior of polar and apolar molecules onto the surface of wetted and nonwetted Amberlite XAD-4.

Table 4. Influence of KCl Concentration c_{KCl}, on Adsorption Capacity of 1,1,1-Trichloroethane onto Nonwetted XAD-4 at 20 °C

c_{KCl}/mol L^{-1}	equilibrium conc of 1,1,1-trichloroethane in the water phase/mol m^{-3}	sorbent loading/mol kg^{-1}	K_F^l (eq 1a)[a]
0	1.04	1.71	1.66
0.2	0.90	1.72	1.80
0.6	0.75	1.73	1.95
1.1	0.49	1.74	2.37
2.3	0.21	1.76	3.44
3.2	0.12	1.76	4.39

[a] Assuming that $1/n_F^g = 0.43$.

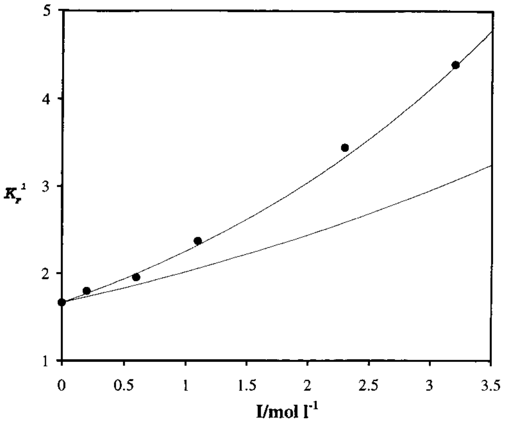

Figure 6. Freundlich constant K_F^l versus ionic strength I for the adsorption of 1,1,1-trichloroethane onto nonwetted Amberlite XAD-4 at 20 °C:—s = 0.305 L mol^{-1} (this work); ● s = 0.193 L mol^{-1} (Gosset, 1987).

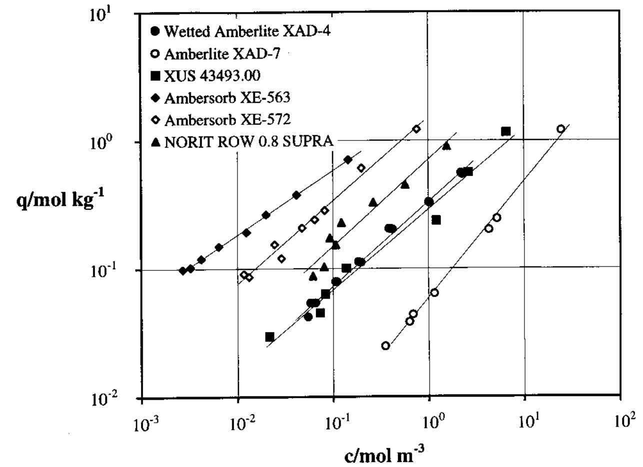

Figure 7. Isotherms for the adsorption of dichloromethane onto wetted Amberlite XAD-4, Amberlite XAD-7, Ambersorb XE-563, Ambersorb XE-572, Dowex XUS-43493.00, and Norit ROW 0.8 SUPRA at 20 °C.

Table 5. Freundlich Constants (Eq 1a) for the Adsorption of Dichloromethane by Several Sorbents at 20 °C

sorbent	K_F^l	$1/n_F^l$
Amberlite XAD-4	0.33 ± 0.02[a]	0.66 ± 0.03
Amberlite XAD-7	0.059 ± 0.006	0.91 ± 0.06
Ambersorb XE-563	1.83 ± 0.17	0.50 ± 0.02
Ambersorb XE-572	1.51 ± 0.36	0.65 ± 0.08
Dowex XUS-43493.00	0.29 ± 0.06	0.63 ± 0.08
Norit ROW 0.8 SUPRA	0.71 ± 0.23	0.68 ± 0.16

[a] 95% confidence limit.

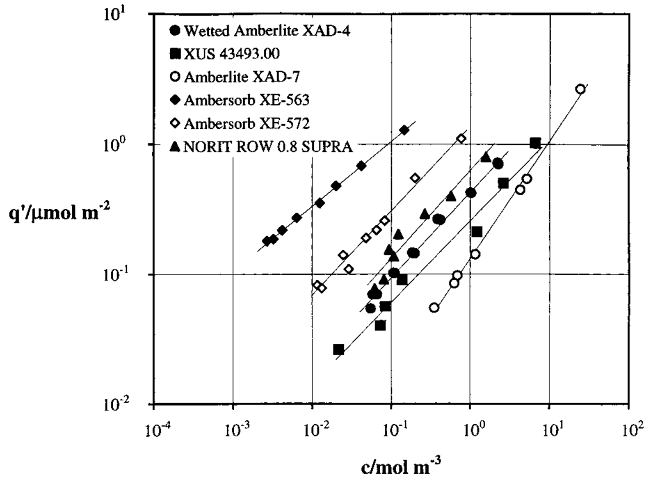

Figure 8. Adsorption isotherms for the adsorption of dichloromethane onto wetted Amberlite XAD-4, Amberlite XAD-7, Ambersorb XE-563, Ambersorb XE-572, Dowex XUS-43493.00, and Norit ROW 0.8 SUPRA at 20 °C. Sorbent loading given per unit of surface area.

capacity. This may explain why Norit ROW 0.8 SUPRA, despite its hydrophilic surface, has such a high adsorption capacity. Amberlite XAD-7 is hydrophilic and has, in addition, only a small amount of micropores, which explains the small adsorption capacity for dichloromethane, observed with this sorbent.

Conclusions

The adsorption of 1,1,1-trichloroethane, 1,1,2-trichloroethane, chloroform, dichloromethane, trichloroethene, *trans*-1,2-dichloroethene, and 2,4-dichlorophenol from an aqueous solution onto nonwetted as well as wetted Amberlite XAD-4 was investigated. Nonwetted and wetted hydrophobic sorbents showed identical adsorption capacities for the strongly apolar hydrocarbons. Thus, the application of a special wetting procedure, as frequently reported in the literature, is not necessary for such hydrocarbons. However, hydrocarbons which are more polar, for example, phenols, are better adsorbed by wetted than by nonwetted hydrophobic adsorbents. Furthermore, it appeared that the adsorption capacity of both wetted and nonwetted Amberlite XAD-4 is predominantly determined by the liquid—solute interaction, which can be expressed in terms of liquid-phase activity.

The addition of salt was found to increase the apparent adsorption capacity of nonwetted Amberlite XAD-4 for 1,1,1-trichloroethane through the so-called salting-out effect. At the conditions applied, a salting-out coefficient of 0.305 L/mol was measured.

Adsorption of dichloromethane onto several synthetic sorbents and activated carbon at 20 °C has been investigated. The adsorption capacity was found to increase with hydrophobicity of the resin and decrease with pore size. The resulting order of increasing adsorption capacity was found to be Amberlite XAD-7 < Amberlite XAD-4 ≈ Dowex XUS 43493.00 < Norit ROW 0.8 SUPRA < Ambersorb XE-572 < Ambersorb XE-563.

Acknowledgment

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Literature Cited

Belfort, G.; Altshuler, G. L.; Thallam, K. K.; Feerick, C. P.; Woodfield, K. L. Selective adsorption of organic homologues onto activated carbon from dilute aqueous solutions, Solvophobic interaction approach. *Fundamentals of Adsorption*; Engineering Foundation: New York, 1983

Cornel, P.; Sontheimer, H. Sorption of dissolved organics from aqueous solution by polystyrene resins—I. Resin characterization and sorption equilibrium. *Chem. Eng. Sci.* **1986**, *41*, 1791−1800.

Daignault, S. A.; Noot, D. K.; Williams, D. T.; Huck, P. M. Review paper: A review of the use of XAD resins to concentrate organic compounds in water. *Water Res.* **1988**, *22*, 803−813.

Gibbs, J. W. *The scientific papers of J. Willard Gibbs*; Dover: New York, 1961; Vol. 1, pp 55−371.

Gmehling, J.; Menke, J.; Schiller, M. *Activity coefficients at infinite dilution:* $C_{10}-C_{36}$ *with* O_2S *and* H_2O*;* Chemistry Data Series Vol. 9-4; Dechema: Frankfurt/Main, 1994.

Gosset, J. M. Measurement of Henry's law constants for C_1 and C_2 chlorinated hydrocarbons. *Environ. Sci. Technol.* **1987**, *21*, 202−208.

Grayson, M., Eckroth, D., Mark, H. F., Othmer, D. F., Overberger, C. G., Seaborg, G. T., Eds. *Kirk-Othmer: Encyclopedia of Chemical Technology*; John Wiley and Sons: New York, 1979; Vol. 5.

Gustafson, R. L.; Albright, R. L.; Heisler, J.; Lirio, J. A.; Reid, O. T., Jr. *Adsorption of organic species by high surface area styrene−divinylbenzene copolymers*; *Ind. Eng. Chem. Prod. Res. Dev.* **1968**, 2, 107−115.

Halsey, G. The role of surface heterogeneity in adsorption. *Adv. Catal.* **1952**, *4*, 259.

Horváth, A. L.; Forrest, W. G. *Halogenated benzenes, toluenes and phenols with water*; Solubility Data Series Vol. 20; Pergamon Press: Oxford, U.K., 1985.

Horváth, A. L., Getzen, F. W., Eds. *Halogenated methanes with water*; Solubility Data Series Vol. 60; Oxford University Press: Oxford, U.K., 1995.

Horváth, C.; Melander, W.; Molnár, I. Solvophobic interactions in liquid chromatography with nonpolar stationary phases. *J. Chromatogr.* **1976**, *125*, 129−156.

Kennedy, D. C. Treatment of effluent from manufacture of chlorinated pesticides with a synthetic, polymeric adsorbent, Amberlite XAD-4. *Environ. Sci. Technol.* **1973a**, *7*, 138−141.

Kennedy, D. C. Macroreticular Polymeric Adsorbents. *Ind. Eng. Chem. Prod. Res. Dev.* **1973b**, *12*, 56−61.

Kroschwitz, J. I., Howe-Grant, M., Eds. *Kirk-Othmer: Encyclopedia of Chemical Technology*; John Wiley and Sons: New York, 1993; Vol. 6.

Paleos, J. Adsorption from aqueous and nonaqueous solutions on hydrophobic and hydrophilic high surface-area copolymers. *J. Colloid Interface Sci.* **1969**, *31*, 7−18.

Parfitt, G. D. *Adsorption from solution at the solid/liquid interface*; Academic Press: London, 1983.

Rixey, W. G. Nonwet adsorbents for the selective recovery of polar organic solutes from dilute aqueous solution. Ph.D. Thesis, University of California, Berkeley, 1987.

Vliet van, B. M.; Weber, W. J., Jr. Comparative performance of synthetic adsorbents and activated carbon for specific compound removal from wastewaters. *J.—Water Pollut. Control Fed.* **1981**, *53*, 1585−1598.

Weast, R. C., Ed. *Handbook of chemistry and physics, 64th ed.;* CRC Press: Bota Raton, FL, 1983.

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