Adsorption from solutions

(Adsorption of phenol by activated carbon)

Understanding the adsorption properties of activated carbons utilized in water treatment processes will be the subject of these experiments.

1. Introduction

Enrichment from the liquid phase at solid/liquid (S/L) interfaces provides the basis of several industrial technologies. When adsorption occurs from the liquid phase, an interface of a new composition may develop, and consequently the energy conditions of the surface change as well. Adsorption at S/L interfaces can be applied to influence the stability of dispersions, which is often a significant step in industrial or lab scale processes. The S/L adsorption phenomenon is also utilised, e.g., in water purification, in solvent recovery and regeneration, in decolouring (in food industries), in the textile industry (dyeing and printing), in ore enrichment (flotation), oil recovery, washing, etc. Further examples are liquid chromatography, heterogeneous catalysis; controlling the size of nanoparticles if synthesised within the interfacial layer. Occasionally, it may be used for determining the surface properties (e.g., surface area) of solid materials (adsorbents, catalysts, fillers in composite materials) that apply in the liquid medium, as S/L conditions may be more relevant to their application than standard nitrogen adsorption measurements.

S/L interactions have significant ecological relevance as well. The fundamentals of adsorption are also a requirement for understanding the processes that occur at the interfaces of soil particles exposed to rainfall, ground water or waste waters, or of particles floating in lakes, rivers or oceans, etc., and the consequences of all these interactions in the natural environment.

The application of porous materials with high surface area (so called adsorbents) e.g., activated carbon, silica gel, zeolites, are based on the results of adsorption methods.

2. Adsorption

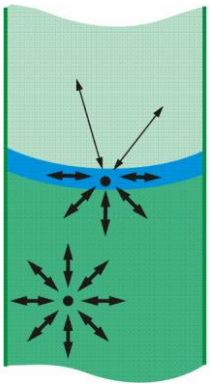

Figure 1 *The resultant of the forces acting on the molecules in the interface is nonzero. Thick arrow: interaction between identical molecules in the same phase; thin arrow: interaction between molecules in neighbouring phases*

In systems consisting of more than one phase a layer of finite thickness called interface will develop between the adjacent phases. The reason for the formation of such interfaces is that the molecules in the outermost ”layer” of a phase are in a different ”environment” on the molecular scale than those in the bulk phase (Fig. 1.). In the bulk phase the forces acting on a molecule are balanced, but on the contrary, on the surface they are unbalanced. The energy of

the molecules in this layer therefore exceeds the energy of those in the bulk. A well-known manifestation of this phenomenon in liquids is the appearance of a meniscus, i.e., capillary action.
When the liquid phase contains more than one component (dissolved material(s) + solvent) the interactions between these components and the surface might be different. That would lead to the surface enrichment of the components showing stronger interaction with the surface sites. The enrichment leading to the development of an interface (surface layer) is called sorption. The interaction between the molecules of the adjacent phases leads to the formation of primary (covalent, Coulombic) or secondary (van der Waals, dispersion) bonds. Enrichment through secondary interactions is called ADSORPTION or PHYSISORPTION. If an electron exchange occurs between the adjacent phases and/or covalent bonds are formed, it is called specific adsorption or CHEMISORPTION.
The thickness of the interface depends on the physicochemical properties of the adjacent layers, varying from a few tenths of a nm in the case of a single layer called also a monolayer (size of a single atom/ion/molecule) up to 10 - 100 nm. The interface bridges the two adjacent phases: it separates and simultaneously connects them. Interfaces may be classified according to the state of the neighbouring phases. From adjoining gas (G), liquid (L) or solid (S) phases L/G, L/L, S/G, S/l or S/S type interfaces may form.
Adsorption is a spontaneous processes, therefore the change of the Gibbs free energy ΔG is negative:.

$$\Delta G=\Delta H-T\Delta S < 0 \qquad (1)$$

where ΔH is the change of enthalpy, ΔS is the change of entropy and T is the thermodynamic temperature (in Kelvin). We recall that S is a measure of disorder. When the freely moving building units (atoms, ions, molecules) from the mobile bulk phase anchor on the solid surface, they lose part of their freedom, i.e., their entropy decreases. Thus $T\Delta S$ term in Eq. 1 is negative. As the process is spontaneous, ΔG is negative. This is possible only if ΔH compensates this ”contradiction”, i.e., it has to be negative. The conclusion is that the adsorption, i.e., the formation of the interfaces is always an exothermic process. Heat will be generated during such processes.
To reach the adsorption equilibrium takes time (Fig. 2). The rate of the equilibration, i.e., the kinetics also depends on the temperature, therefore adsorption processes are preferably studied at constant temperature.

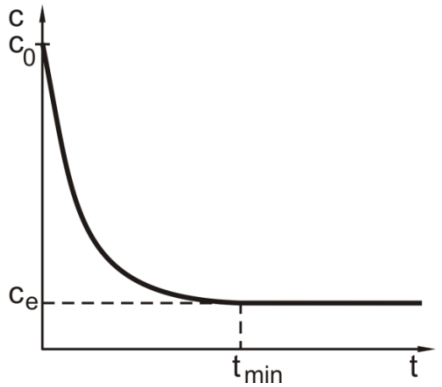

Figure 2: The time dependence of the concentration: equilibrium concentration and the minimum contact time (t_{min})

Adsorption is the enrichment of atoms/ions/molecules from a gas, liquid, or dissolved solid to a surface. To enhance this phenomenon the volume ratio of the interface needed to be

increased, which associated with the specific surface area of the adsorbent. This can be achieved by grinding or more effectively by the enhancement of the porosity.

3. Adsorption from liquid phase

Hereafter we are going to discuss binary solutions containing only a small amount of solute (dilute solutions). The mechanism of the adsorption is complex, because the coverage by liquids is always complete, i.e., when the solid is in contact with enough liquid (the minimum is the amount needed for the formation of a complete adsorbed layer) all the surface sites are occupied. However, this does not mean that the actual distribution of the liquid molecules corresponds to an energy minimum, i.e., competition takes place. The adsorption equilibrium is achieved through exchange of molecules in the bulk liquid and molecules already in the interface. The composition of the surface layer is determined by the interactions of the A and B molecules within the liquid (A-A, B-B, A-B) and in the adsorbed phases, and their interactions with the surface sites.

The time needed to reach the equilibrium is based on previously made kinetic measurements. The diffusion in liquid phase is quite slow. The contact time can be shortened by mixing or shaking.

The adsorption is characterized by the isotherms and their parameters deduced from various fitting models. In liquid adsorption isotherms (Fig. 3.) the adsorbed amount (n_a) is shown as the function of the equilibrium concentration (c_e). They can be measured either by static (batch) or dynamic (flow) methods. Direct determination of the composition of the adsorbed layer nevertheless is fairly challenging. Therefore, indirect methods are widely applied: the composition change in the free bulk liquid combined with a material balance is used to determine the amount and composition of the adsorbed layer. This can be done correctly only if we are assured that the change in the composition of the free bulk liquid is caused strictly by adsorption alone. That is, neither the liquid nor any of its components should dissolve the solid or any impurities of the solid, no chemical reaction occurs between any of these players, evaporation loss is eliminated, etc. Any suitable method for monitoring the composition of the liquid mixture (UV absorption, RI, etc.) can be used. In the case of multicomponent mixtures, particularly gas or liquid, chromatography assisted concentration determination is recommended.

In case of dilute solutions the concentration is often given in mol/L or g/L units. If a solid with m mass and a binary liquid with concentration c_0 and volume V_0 interact with each other, as it was discussed previously, the two component (solute + solvent) will compete for the surface sites.

Based on the mass balance of the system, after reaching the equilibrium where the equilibrium concentration is c_e and the free volume of the liquid phase is V_e , the adsorbed amount can be calculated as

$$m_a = \frac{c_0 V_0 - c_e V_e}{m} = \frac{(c_0 - c_e)V}{m} \qquad (2)$$

The volume may change during the adsorption due to swelling. We have to make sure no evaporation happens. If the solid phase does not swell, i.e., V_0=V_e, the expression becomes simpler (last term in eq. 3).

The shape of the typical isotherms might be of L or S shaped or stepwise (SW). (Fig. 3.). The strength of the interaction is influenced by the character of the surface, the properties of the solute and the solvent together.

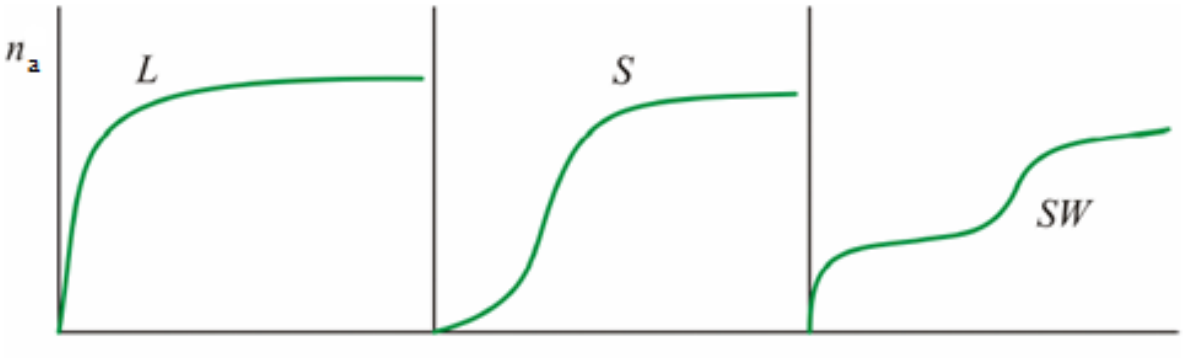

Figure 3: Types of adsorption isotherms for dilute solutions

The initial section of the isotherm is related to the strength of the interaction between the solid and the adsorbate. L shaped isotherms are obtained when this interaction is strong. S shaped isotherms are measured when the interaction between the solute and the solvent is stronger than between the solute and the surface. SW type isotherms generally indicate bilayer adsorption of assembled adsorbates. It is typical in case of surfactant molecules: the first layer adsorbs in an oriented way on the solid surface: if the surface is typically polar the adsorbates are anchored with their polar end. Thus, the completion of the monolayer converts the surface nonpolar. The second layer develops by the self-assembly of the amphiphilic molecules: the nonpolar end interacts with the nonpolar adsorbate.

4. Interpretation of the experimental data, evaluation of the adsorption isotherms

Evaluation of adsorption isotherms may go further that the simple presentation of the adsorption isotherms. This is based on adsorption models. The most frequent models are the Langmuir or Freundlich models.

The former developed by Irving Langmuir is based on two hypotheses. The conditions of this very simple and idealistic model are that i) the surface is energetically homogeneous (all the surface site – probe molecule interactions yield the same adsorption energy); and ii) the adsorption is limited to a single layer (monolayer). Therefore, the adsorbed amount – equilibrium concentration relation can be given as

$$m_a = \frac{m_m \cdot K \cdot c_e}{1 + K \cdot c_e} \qquad (3)$$

where m_m is the amount of adsorbed material needed to complete a closely packed monolayer on the surface and K is the equilibrium constant of the adsorption process. These two parameters can de derived if this hyperbolic function is fitted to the isotherm. We may recall that K is temperature dependent, i.e., also reflects the temperature dependence of the adsorption process.

Instead of hyperbolic fitting a transformed version of equation (3) is preferred as the parameters can be obtained from a linear fit (Figure 4):

$$\frac{c_e}{m_a} = \frac{1}{m_m \cdot K} + \frac{c_e}{m_m} \qquad (4)$$

However the assumptions of the model are very strict and seldom met, the model os widely used. Its great advantage is that it is based on a clear and simple physical model and its parameters can therefore be related directly to this physical picture.

For fitting the linearised form of the equation is used:

This way the quotient calculated from the measured data $\frac{c_e}{n_a}$ is shown in the function of c_e

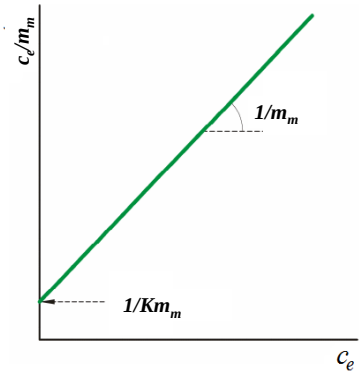

Figure 4. Derivation of the Langmuir parameters from the linearised plot

In case of very dilute solutions (c → 0) the nominator in eq. 3 1+Kc ≈ 1. Therefore, the isotherm equation simplifies to

$$m_a = K_H c_e \tag{5}$$

where K_H is the Henry constant. This Henry type isotherm is especially typical for environmental samples.

The advantage of the Langmuir isotherm is also is its disadvantage. Its constrains (surface sites with identical binding energy, only single layer adsorbed) cannot always be met. Models for surfaces with heterogeneous binding sites are also required. One of such models is the Freundlich model. It is presumed in this model that the energy of the surface sites show a Gaussian distribution. The isotherms can be modelled also by a two-parameter equation. These fitting parameters are *k* and *b>1* without any physical interpretation:

$$m_a = k \cdot c_e^{\frac{1}{b}} \tag{6}$$

Again, for fitting a linear form of the equation is used:

$$\ln m_a = \ln k + \frac{1}{b} \ln c_e \tag{7}$$

This way k can be calculated from the intercept, *b'* from the slope of the logarithmic plot.

4. Adsorption of phenol on activated carbon

4.1. Activated carbon

Activated carbon is a porous material with a hierarchical porous structure (Figure 5). Its main component is carbon, but depending on its precursor, it may contain H, O, inorganic salts or oxides. It is produced from precursors of high carbon-content (coal, bones, lignocellulosic materials like peat, wood, or from polymers, etc.). The best quality carbons are obtained from fruit stones, e.g. from coconut. Their surface properties depend on their raw material and the technology of their preparation.

Due to their porous structure their specific surface, i.e., the surface area of 1 g carbon is outstandingly high (400- 1600 m^2/g). Their pores can be categorised by their size:

macropores: width exceeding 50 nm,
mesopores: width in the range 2–50 nm,
micropores: width narrower than 2 nm.

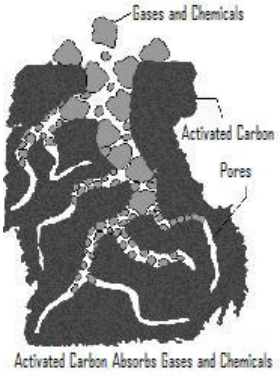

Figure 5. Pore hierarchy in activated carbons (http://www.innofresh.com/activated-carbon/)

The width means diameter in case of cylindrical pores and the distance between the pore walls in case of slit shaped pores. Outstandingly high surface area materials are typically microporous. Due to their high specific surface area, outstanding adsorption capacity and tuneable pore structure they are general adsorbents. A large amount of activated carbon is used in water purification.

4.2. Phenol

Phenol and its derivatives are widely used intermediers pesticide, medicine, paint, etc. in synthesis. During the degradation of these materials phenol or its derivatives can get to the environment. That is why they are one of the most frequent pollutants of water. They have very unpleasant taste and smell already in very small concentration. Their halogenated versions may be carcinogenic. Phenols are cumulated in animals and humans because most of the living cannot degrade it. Their removal from drinking water is of crucial importance.

Phenol is a weak acid, its dissociation is shown in Fig. 6. (*pKa* at 20 °C is 9.89). When adsorbed on a flat surface its cross section, i.e., the area occupied by a single molecule is 0.30–0.42 nm^2.

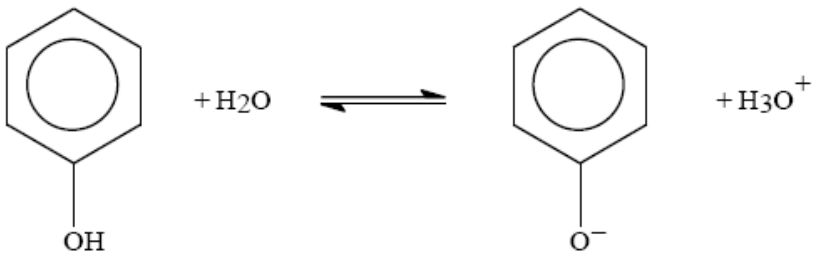

Figure 5.: Dissociation of phenol

Phenol is an aromatic compound, therefore it can be easily detected by UV spectroscopy.

4.3. UV-Vis spectroscopy

When a molecule is irradiated by light and the energy of the light is equal to the difference between an exited and the ground state, the molecule can absorb the light and get to an excited state. This phenomenon is called a**b**sorption. Ultra violet- visible (UV-Vis) absorption spectroscopy is based on this phenomenon. In UV-Vis spectroscopic observations samples are irradiated by light with a continuously changing wavelength λ, and the transmitted radiation is examined as a function of the wavelength. Transmittance (*T*) or absorbance (*A*) are used for

quantitative characterisation. Transmittance is the ratio of the transmitted (I) and the incident intensity (I_o) of the light:

$$T = \frac{I}{I_0} \tag{8}$$

Absorbance is defined as

$$A \equiv -lg\,T = lg\,\frac{I_0}{I} \tag{9}$$

The $T(\lambda)$ or $A(\lambda)$ functions are the UV-Vis spectra of a molecule. UV-Vis spectroscopy can be used not only for structural analysis but also for quantitative analytical purposes. We can use the concentration dependence of the absorption to determine the composition of solvents. According to the Lambert-Beer law the absorbance is proportional to the concentration

$$A = \varepsilon \cdot c \cdot l \tag{10}$$

where ε is the molar absorption coefficient [e.g., $dm^3mol^{-1}cm^{-1}$], c is the concentration [e.g., mol dm^{-3}] and l is the path of the light, i.e., the thickness of the examined sample [e.g., cm].
In the λ range above 200 nm numerous organic and inorganic compounds can be investigated. Examples are organic compounds having π-bond(s) or free electron pair (-CO, -CN, $-NO_2$ functional groups) or loose nonbonding electrons (containing Cl, Br, I, S, Se atom), conjugated double bonds or complexes of transient metals. Materials showing no absorption, such as saturated hydrocarbons (e.g. hexane), water or ethanol are the good solvents for these studies. For quantitative analysis an *A(c)* calibration curve has to be determined in advance.
During the lab practise a SPECORD 200 type spectrophotometer will be used, which operates between 190-1100 nm. The light sources in the UV and visible light range are a deuterium lamp and a halogen lamp respectively.

5. Experimental determination of isotherms

For measuring adsorption isotherms in batch measurements two typical methods are used. Theoretically we either can use a fixed solution volume/adsorbent mass ratio (*V/m)* systematically changing the concentrations, or we use only one concentration (c_0), and systematically change the *V/m* ratio systematically. For this measurement the second option is selected. Concentrations can be determined with various methods depending on the chemical properties of the solute. It is important to check the pure solvent as well to confirm the lack of dissolution of any contaminant from the solid disturbing the concentration analysis.
If a solution with c_0 concentration is added to a solid material with m mass, the concentration is going to decrease continuously until reaching the equilibrium. (Fig.2.). If we can exclude vaporisation, the liquid phase do not solve any contamination from the solid, and the solid do not swell, then the volume V is constant. Then any change in the concentration can be attributed to the adsorption. The amount adsorbed by 1 g of solid can be calculated with Eq. 2.

6. Determination of phenol adsorption capacity of the activated carbon

During the laboratory practise phenol adsorption capacity of commercial activated carbons are to be examined.
Carbons with known surface area will be provided.
For determining the adsorption isotherm, 20, 40, 60, 80, 100 mg carbon (use an analytical balance) should be measured into a sealable bottles. 20 cm^3 phenol solution of 5 mM concentration should be added to each bottle. In all the cases two parallel samples should be

prepared. In one additional bottle 100 mg carbon and 20 cm^3 distilled water and a second one 20 cm^3 phenol solution with 5 mM concentration without any carbon should be added. These latter two samples will help to control that neither dissolution from the carbon no adsorption of phenol on the glass wall of the bottle disturbs the measurements. After closing the bottles it should be shaken till the equilibrium. In our case the contact time will be 1 week. After 1 week the equilibrium concentration should be determined by UV-Vis spectroscopy.

The calibration diagram, i.e. an $A - c$ diagram should be measured at 5 different concentrations including c=0 (pure water). Based on the plot a concentration region where the relation is linear can be selected. All the equilibrium concentrations should be detected in this range. If the equilibrium concentration of any of the samples is beyond this region samples should be diluted. Volumetric flasks should be used for the dilution.

The phenol adsorption isotherm should be plotted and its parameters should be derived from the linear plots by both models. Fitting procedure also includes the determination of the regression of the straight lines.

From the parameters of the Langmuir plot the surface area occupied by the phenol molecules should be calculated. Compare this area to the surface area of the activated carbon and calculate the surface coverage in %.

Worksheet 1.
Data for the calibration curve

Concentration of phenol stock solution:

Absorbance of the calibration points:

dilution [x]	concentration [mol/dm^3]	Absorbance

The equation of the linear calibration:
Regression:

Worksheet 2.
For the adsorption isotherm

Activated carbon sample:

Surface area of the activated carbon:

Concentration of phenol stock solution:

Temperature:

Contact time:

	Mass of the carbon [g]	Volume of the phenol solution [ml]	Concentration of phenol stock solution (c_0) [mol/dm^3]	Measured absorbance	Calculated equilibrium concentration (c_e) [mol/dm^3]
1.					
2.					
3.					
4.					
5.					
Stock solution					
'Background' sample			0		