

Polymeric Materials

Faculty of chemistry

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(based on polish version created by prof. AW Trochimczuk)

Exercise no. 2

Sorption of phenols

The purpose of this exercise is to determine the relationship between the hydrophilicity of phenols, and their sorption on selected commercial polymeric sorbents (Amberlite XAD - 4 and Amberlite XAD - 7).

The major sources of phenolic waste are petroleum refineries, petrochemical industry, steel mills, coke oven plants, coal gas, synthetic resins, pharmaceuticals, paints, plywood industries and mine discharge. Phenolic waste imparts some carbolic odors to river water and is also toxic to fish and human beings. Contamination of surface water and groundwater with aromatic compounds is one of the most serious environmental problems humanity faces today. Owing to its acute toxicity and good solubility, phenol has already been listed as one of the top priority contaminants and also the most important substructure of potentially carcinogenic pollutants discharged from fine chemical plants¹.

Adsorption is the process in which matter is extracted from one phase and concentrated at the surface of a second phase. Adsorption technique is widely used for removal of toxic organic contaminants from aqueous streams. Adsorption is caused by London Dispersion Forces, a type of Van der Waals Force which exists between molecules. The interactions acts in a similar way to gravitational forces between planets.

Sorption is a phenomenon where an increase of the concentration on the surface and the driving force of this process compensate the unbalanced surface forces. Minimum surface energy is achieved by coating the surface with a layer of adsorbed molecules. Sorption phenomenon are described by nature of the interaction between the surface of the sorbent (surface area of the material, typically hundreds to thousands of square meters per 1 gram of dry sorbent) and the sorbate molecule (dissolved in the liquid phase=water) which is adsorbed on the sorbent's surface area.

These interactions may reveal physical and chemical characteristics. The first one is the weak, non-specific, due to van der Waals forces, as well as London's. The second is the impact of a stronger, directional, for example, dipole-dipole, charge transfer interaction, hydrogen bonding. Sorption caused by the first type of interaction is physical sorption. It is reversible: desorption takes place at an elevated temperature or by changing the interaction, for example by elution of the sorbent solvent (methanol, acetonitrile). Sorption caused by second of these effects is called chemisorption and is not always a reversible process.

The distribution of an organic solute between sorbent and solvent phases results from its relative affinity for each phase, that in turn relates to the nature of forces which exist between molecules of the solute and those of the solvent and sorbent phases. The type of interaction depends on the nature of the sorbent as well as the physio-chemical features of the sorbate - hydrophobic or polar at various degrees.

¹ Journal of Hazardous Materials B128 (2006) 123–129, Synergistic adsorption of phenol from aqueous solution onto polymeric adsorbents, Zhang W. Ming, Chen J. Long*, Pan B. Cai, Zhang Q. Xing, B. Zhang

The sorption capacity of a given sorbent may depend on a series of properties, which are grain-size distribution, specific surface area, cation exchange capacity, pH, organic matter or organic carbon content, and mineral constituents.

Weber² summarized the possible interactions between solute and sorbent included into three loosely defined categories of sorption: physical, chemical, and electrostatic.

The physical sorption processes involve interactions between dipole moments (permanent or induced) of sorbate and sorbent molecules. The relatively weak bonding forces associated with physical sorption are often amplified in the case of hydrophobic molecules by substantial thermodynamic gradients for repulsion from the solution in which they are dissolved.

Chemical interactions involve covalent bond and hydrogen bond.

Finally, electrostatic interactions involve ion–ion and ion–dipole forces. In a more detailed way, the type of interactions and the approximate values of energy associated are: 163 van der Waals interactions ~4–8 kJ/mol, hydrophobic bonding ~4 kJ/mol, hydrogen bonding ~2–40 kJ/mol, charge transfer, ligand-exchange and ion bonding 40 kJ/mol, direct and induced ion–dipole and dipole–dipole interactions ~2–29 kJ/mol and chemisorption covalent bond ~60–80 kJ/mol.³

For a commercially available polymeric adsorbent, such as XAD4, it is generally known that van der Waals interaction is the main force to drive phenol molecules from bulk solution to adsorbent phase

A large number of sorbents are available, and the most frequently groups of sorbents are being used:

- chemically modified silica gel,
- polymer sorbents,
- graphitized or porous carbon.

AMBERLITE XAD^{TM4} polymeric adsorbents are porous spherical polymers based on highly crosslinked, macroreticular polystyrene, aliphatic, or phenol-formaldehyde condensate polymers. Their high internal surface areas can adsorb and then desorb a wide variety of different species depending on the environment in which they are used.

For example, in polar solvents such as water, polymeric adsorbents exhibit non-polar or hydrophobic behavior and so can adsorb organic species that are sparingly soluble. This hydrophobicity is most pronounced with the styrenic adsorbents. In non-polar solvents, such as hydrocarbons, etc. most adsorbents exhibit slightly polar or hydrophilic properties and so will adsorb species with some degree of polarity. This polarity is most pronounced with the acrylic adsorbents and the phenolic adsorbents.

Purification strategies are developed to utilize these performance characteristics. In capture/concentration mode, AmberliteTM XADTM media provide an excellent first purification step in the recovery of phenolic compounds or chlorinated hydrocarbons. In some applications XAD resins perform decolorization. AmberliteTM XADTM adsorbents can be used in both, batch and (preferably) column operations.

² W. J. Weber, P. M. Mc Ginley, and L. E. Katz, Water Res. **25**, 499, ~1991!.

³ Alessandro Delle Site, J. Phys. Chem. Ref. Data, Vol. 30, No. 1, 2001

⁴ <http://www.amberlyst.com/xad.htm>

| AMBERLITE™ | Matrix | Surface area (m ² /g) | Av. Pore diameter (Å) | Mean diam. (μ) | UC D90/D40 | Applications |
|-----------------------------------|-----------------|----------------------------------|-----------------------|----------------|------------|--|
| XAD™4 | pStyDVB* | 750 | 100 | 640 | 1.6 | Removal of aromatic hydrocarbons such as phenols and pesticides from wastes. High surface area and small pores. Ideal for the extraction of smaller molecules such as phenol. Hydrophobic. |
| XAD™16N | pStyDVB* | 800 | 150 | 700 | 1.6 | Removal of aromatic hydrocarbons such as phenols and pesticides from wastes or polar solvents. High surface area and medium sized pore for the adsorption of large color bodies. Excellent regenerability. Hydrophobic. |
| XAD™1180N | pStyDVB* | 500 | 400 | 530 | 1.6 | Removal of very large organic molecules from aqueous solutions or polar solvents. Hydrophobic. |
| XAD™1600N | pStyDVB* | 800 | 150 | 400 | 1.2 | Removal of aromatic hydrocarbons such as phenols and pesticides from wastes or polar solvents. Monodisperse. Low swelling between solvent and aqueous solutions. High surface area, excellent separation of different organic species in chromatographic processes. Hydrophobic. |
| XAD™7HP | Aliphatic ester | 500 | 450 | 560 | 1.7 | Adsorption of ketones, esters and aliphatic compounds from polar solvents. Removal of polar compounds from non-aqueous solvents. Purification of bleach plant effluents from kraft pulp mills. Hydrophilic. |
| XAD™761 | Formo-phenolic | 200 | 600 | 700 | 1.5 | Removal of high molecular weight water soluble color bodies aqueous solutions such as glycerol or fermentation broth. Contains phenolic hydroxyl and methylol groups. Hydrophilic. |
| *pStyDVB = Polystyrene DVB | | | | | | |

<http://www.amberlyst.com/literature/a4/xad7hp.PDF>

<http://www.amberlyst.com/literature/a4/xad4.PDF>

<http://www.amberlyst.com/xad.htm>

<http://www.amberlyst.com/literature/a4/xad4.PDF>

<http://www.amberlyst.com/xad.htm>

MANUAL INSTRUCTION

1. Put swollen resins into a centrifuge bottles, balance them and spin them at speed 3000 rpm/min for 5 minutes.
2. Weigh the specified amount of sorbent (tab.2, 3) leading to the numbered small bottles (1-6) and 7, 8 large bottles
Small Erlenmeyer flask from 1 to 3 (XAD – 4),
large bottles 7 (XAD – 4),
large bottle 8 (XAD - 7)

(Note: Add centrifuged polymer based on dry weight of 0.1 g and 0,5 g).

A. Determination of relationship between the hydrophilicity of phenols and sorption properties of commercial polymeric sorbents (Amberlite XAD-4 and Amberlite XAD-7).

1. Dispense into each Erlenmeyer flask.
20 cm³ of phenol solution (for Erlenmeyer flask 1 and 4),
20 cm³ 2,6-dimethyl phenol (for a Erlenmeyer flask 2 and 5)
20 cm³ hydroquinone (to a Erlenmeyer flask 3 and 6), each at a concentration of 0.5 mM .

B. The sorption kinetics study

Adsorption kinetics is important for understanding the uptake rates of pollutants on the surfaces of adsorbents and determining the equilibrium times of adsorptions. The changes of phenols removal efficiency with contact time for various adsorbents should be explained.

1. To the large bottles of 500 cm³ add 250 cm³ of a solution of phenol having a concentration of 0.5 mM (**Note: Add dry polymer based on dry weight of 0.5 g.**)
2. Shake the bottles and withdrawn a sample volume of 3 ml at specified times (table 4) ie., after 10, 15, 30, 45, 60 and 90 minutes, and place them in the numbered test tubes.
3. Measure the concentration of phenol's after the specified time and λ ($\lambda = 270$ nm). Note in the table 2.
4. Measure the concentration of each phenols at the wavelength (phenol $\lambda = 270$ nm, 2,6-dimethylphenol $\lambda = 269.9$ nm for and $\lambda = 289.4$ nm for hydroquinone). Note in the table 4.

Determination of each phenol concentration by UV-VIS Absorption Spectroscopy

The phenol's concentration after sorption are determined quantitatively by the spectrophotometric method using a UV-VIS spectrophotometer (TABLE 1)

The Beer-Lambert law (or Beer's law) is the linear relationship between absorbance and concentration of an absorbing species. The general Beer-Lambert law is usually written as:

$$A = \epsilon \cdot b \cdot c,$$

Where:

A is the measured absorbance,

ϵ is a wavelength-dependent **absorptivity coefficient** (sometimes called, also knows as molar absorptivity),

b is the quartz cells cell-path length, 1 cm

c is the analyte concentration.

When working in concentration units of molarity, the Beer-Lambert law is where is the wavelength-dependent molar absorptivity coefficient with units of $M^{-1} cm^{-1}$.

CALCULATION

A sorbing system has a sorption capacity, *S*, defined as the ratio of the mass of sorbate to the unit mass of sorbent.

Sorption calculate as :

$$S = \frac{c_0 - c_T}{m_{DRY}} \quad (1) \quad \text{or} \quad S = \frac{c_0 - c_T}{m_{DRY}} \quad (2), \text{ [mmol/g], [mg/g], [mmol/ml]}$$

gdzie:

c_0 – initial concentration of phenol,

c_t – equilibrium concentration of phenol

m_{dry} – amount of polymer

v- volume of phenol solution, ml

Water regain is being determined from the relation between wet and dry%

$$W = \frac{m_{wet} - m_{dry}}{m_{dry}} = \frac{m_{wet}}{m_{dry}} - 1, \left[\frac{gH_2O}{g} \right]$$

W – water regain [g H₂O/g dry resin]

m_{wet} – mass of swollen resin after centrifugation [g]

m_{dry} – mass of dry resin [g]

The content of the polymer in the swollen gel % = $\frac{m_{dry}}{m_{wet}} \times 100\%$

The rate constants should be calculated using the various models (viz. pseudo-first-order, pseudo-second-order models)⁵, tab.5.

The report should include the completed tables with measurements, the calculated value sorption of phenols, a dependency graph (kinetic models) for phenol on both sorbents, as well as the explanation of the observed phenomena.

⁵ J Hazard Mater. 2008 , 15;157(2-3):293-9.

2.2.3. Adsorption kinetics modeling

In order to investigate the adsorption mechanism, the pseudo-first-order adsorption, the pseudo-second-order adsorption and the intraparticle diffusion models were used to fit kinetics experimental data. The weighted sample (200 mg) of the apatite was mixed with a 100 ml phenol solution (20 mgL^{-1}) to carry out adsorption studies in a batch mode.

2.2.3.1. *Pseudo-first-order model.* The pseudo-first-order rate expression of Lagergren is usually described by the following equations (Srihari and Das, 2008):

$$\frac{dq_t}{dt} = k_1 (q_{e,1} - q_t) \quad (2)$$

where q_e and q_t are the amounts of phenol adsorbed on the apatite at equilibrium and at time t , respectively, and k_1 is the

rate constant of pseudo-first-order sorption. Integrating and applying the boundary condition, $t = 0$ and $q_t = 0$ to $t = t$ and $q_e = q_t$, Eq. (2) takes the following form:

$$\log(q_e - q_t) = \log q_{e,1} - \frac{k_1}{2.303}t \quad (3)$$

The rate k_1 was obtained from slope of the linear plots of $\log(q_e - q_t)$ against t .

2.2.3.2. *Pseudo-second-order model.* The sorption data were also analyzed in terms of a pseudo-second-order mechanism by the following equation (Wu et al., 2001; Antonio et al., 2007):

$$\frac{dq_t}{dt} = k_2 (q_{e,2} - q_t)^2 \quad (4)$$

Integrating and applying the boundary condition, $t = 0$ and $q_t = 0$ to $t = t$ and $q_e = q_t$, Eq. (4) takes the form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e,2}^2} + \frac{1}{q_e}t \quad (5)$$

If the second-order kinetics model is applicable, the plot of t/q_t against t of Eq. (5) should give a linear relationship from which the constants $q_{e,2}$ and k_2 can be determined.

Table 1.

Initial solutions of sorbates

| | Concentration (Units) | Wavelength | ABS | ϵ |
|--------------------|-----------------------|------------|-----|------------|
| PHENOL | 0,5 | 270 | | |
| 2,6 DIMETHYLPHENOL | 0,5 | 269,9 | | |
| HYDROQUINONE | 0,5 | | | |

TABLE 2. Sorption after 1 hour

| NO | RESIN | WATER REGAIN G/G | RESIN DRY, G | | RESIN SWOLLEN (WET), G | | KIND OF PHENOL 20 ml | ABS. after sorption (time=1 h) | C_{eq} | SORPTION (UNITS) |
|----|-------|------------------|------------------------|---------------|------------------------|---------------|----------------------|--------------------------------|----------|------------------|
| | | | required sample weight | weight sample | required sample weight | weight sample | | | | |
| 1 | XAD-4 | | 0,1 | | | | PHENOL | | | |
| 2 | XAD-4 | | 0,1 | | | | 2,6-dimethylphenol | | | |
| 3 | XAD-4 | | 0,1 | | | | hydroquinone | | | |
| 4 | XAD-7 | | 0,1 | | | | PHENOL | | | |
| 5 | XAD-7 | | 0,1 | | | | 2,6-dimethylphenol | | | |
| 6 | XAD-7 | | 0,1 | | | | hydroquinone | | | |

C_{eq} – concentration after 1 hour

KINETIC STUDY OF PHENOL SORPTION

The kinetics of sorption describes the solute uptake rate, which in turn governs the residence time of sorption reaction. It is one of the important characteristics in defining the efficiency of sorption.

Students should pay attention WHAT IS sorbate ?

Sorbate used

Table 3.

| NO | RESIN | WATER REGAIN, G/G | RESIN, G | | | | KIND OF PHENOL 250 ml |
|----|-------|-------------------------|------------------------------|------------------|------------------------------|------------------|---------------------------------|
| | | | DRY | | WET | | |
| | | | required sample weight | weight sample | required sample weight | weight sample | |
| 7 | XAD-4 | | 0,5 | | | | |
| 8 | XAD-7 | | 0,5 | | | | |

Absorption UV-VIS

Table 4.

| TIME | XAD-4 | | | XAD-7 | | |
|--------|------------|-------------------|---------------------|------------|-------------------|---------------------|
| | ABSORPTION | C _{TIME} | SORPTION (UNITS) | ABSORPTION | C _{TIME} | SORPTION (UNITS) |
| 10 MIN | | | | | | |
| 15 MIN | | | | | | |
| 30 MIN | | | | | | |
| 45 MIN | | | | | | |
| 60 MIN | | | | | | |
| 90 MIN | | | | | | |

Tab.5 Kinetic parameters for the sorption onto XAD resins

| MODELS | COEFFICIENTS | R ² |
|---------------------|------------------------------------|----------------|
| PSEUDO FIRST ORDER | K ₁ = Q _E | |
| PSEUDO SECOND ORDER | K ₂ = Q _E | |