

ADSORPTION IN SOLUTION

Objective

The aim of this experiment is to study the adsorption of a dye solution by an adsorbent solid such as zeolite, silica gel, activated carbon and then test the validity of certain adsorption isotherm.

Principle and Theory

Adsorption is a process that uses special solids to remove substances from either gaseous or liquid mixtures. It is an industrially important process occurs with the attachment of the liquid or gas particles onto a solid surface. The special solids that gas or liquid particles attached are called **adsorbent**. The substances adsorbed are called **adsorbate**. Adsorption is a phenomenon occurs at the surface; the molecules are taken up by the surface. It should not be confused with absorption. Adsorption and absorption are two different processes; the molecules are taken up by the volume in absorption, not by surface i.e. the solute is dissolved in the bulk material in absorption. Adsorption can be classified into two different groups depending on the type of the interaction between the adsorbed molecule and the solid surface.

- *Physisorption*; Physisorption is caused mainly by intermolecular forces (Van der Waals) and electrostatic forces between adsorbate molecule and the atoms which compose adsorbent surface. It will occur when the intermolecular attractive forces between adsorbent and adsorbate are greater than those existing between the molecules of the adsorbate itself.
- *Chemisorption*; Chemisorption is the result of chemical interaction between adsorbate and adsorbent. The adsorbate sticks to the solid by the formation of a chemical bond with the surface. This interaction is much stronger than physisorption. Unlike in physisorption only monolayer adsorption is observed.

Also it should be noted that the same adsorbate which under the conditions of low temperature, undergoes only physisorption, may sometimes exhibit chemisorption at higher temperatures, and both phenomena may occur at the same time.

Adsorption is reversible process. The reverse of this process is called as desorption. There exists equilibrium between adsorption and desorption process. Adsorption is a function of the concentration of the adsorbate and temperature of the solution.

Since adsorption occurs on the surface, the surface properties of adsorbents are quite important. Large specific surface area is preferred in order to have a large adsorption capacity which is the most important characteristics of an adsorbent. Adsorption capacity is the amount of adsorbate taken up by the adsorbent per unit mass (or volume) of adsorbent. Major types of adsorbents in use are: activated alumina, silica gel, activated carbon, molecular sieve carbon, molecular sieves zeolites and polymeric adsorbents.

Silica Gel is a porous, amorphous form of silica (SiO_2). Due to its unique internal structure Silica gel is radically different to other SiO_2 -based materials. It is composed of a vast network of interconnected microscopic pores. This amorphous material comprises spherical particles 2-20 nm in size which aggregate to form the adsorbent with pore size in the range of 6-25 nm. Surface areas are in the range of 1 00-850 ~ding on whether the gel is low density or regular density.

Zeolites are crystalline structures. They have large internal cavities where molecules can adsorbed. They are porous aluminosilicates, because of its cristalline nature the pores and cavities are at the same size and depending on the size of the openings the can adsorb molecules readily, slowly or not at all, thus they are called as molecular sieves which defined as adsorbing of the molecules at certain sizes while rejecting larger ones. Zeolites have large open spaces and cages in their structures that form channels. These channels allow the easy movement of ions and molecules into and out of the structure. More than 150 types of synthetic zeolites are known, the most important commercial types are type A and X, synthetic mordenite and their ion-exchanged varieties.

Activated carbon is basically amorphous carbon based material exhibiting a high degree of porosity and interparticulate surface area. Large surface area of activated carbon provides excellent adsorbent characteristics. The surface area per gram of material can range 500 to 1200 m^2 . Because of its good adsorption properties they are useful in many industrial processes. Filtration, purification, deodorization, decolorization and separations are the examples of these processes.

In industry, adsorption is a very important process. It is used in gas-phase and liquid-phase applications. Removal of organic compounds from water or organic solutions, colored impurities from organics and removal of moisture dissolved in gasoline are the examples of liquid phase systems. Removal of water vapor from air and other gases, sulfur compounds

form natural gas and the recovery of some valuable solvent vapors from their mixtures with air and gases can be given as example of the gas-phase systems. Adsorption techniques are widely used to remove certain types of pollutants in wastewater treatment processes. With the selection of a proper adsorbent, the adsorption process can be a promising technique for the removal of contaminants.

Adsorption Equilibrium

A large majority of adsorption operate through equilibrium adsorption of mixture. The amount of gas or liquid adsorbed, n^a by mass, per gram of solid, m^s , depends on the specific surface area of the solid, the equilibrium solute concentration in the solution, C_{eq} (pressure for gas phase adsorption), the temperature, and the nature of the molecules involved. For the given system at constant temperature, it is possible to write the adsorption isotherm equation as follows

$$q_{eq} = n^a / m^s = f(C_{eq}) \quad (1)$$

where q_{eq} is the amount of adsorbate per unit mass of adsorbent.

The most common way of getting information about a given system is to take experimental measurements, at constant temperature, of the amount of adsorbate on the surface as a function of concentration (or pressure) and then draw a plot of q_{eq} (the amount of adsorbate per unit mass of adsorbent) versus C_{eq} (the equilibrium solute concentration in adsorption from solution). Such a graph is called an adsorption isotherm.

The Freundlich Isotherm

It applies over a limited range of concentrations and is somewhat better for liquid – solid systems. It has the form of

$$q_{eq} = n^a / m^s = K. (C_{eq})^a \quad (2)$$

where, n^a = Amount of the adsorbate (grams) & m^s = Amount of the adsorbent

In Eqn (2) K and a are constants.

The Langmuir Isotherm

This is an equation derived by theoretical considerations upon some simplifying assumptions and explains the gas solid systems better, it can however be applied to some simple liquid – solid systems as well.

The theory of Langmuir is restricted to cases where only one layer of molecule can be adsorbed on the surface. As mentioned before, in the case of chemisorption monolayer adsorption is usually observed. The monolayer adsorption is distinguished by the fact that the amount adsorbed reaches a maximum value at moderate concentrations (corresponding a complete coverage of the surface of the adsorbent by a layer of adsorbed molecules which is one molecule thick only), and remains constant with further increase in concentration. The equation of Langmuir as derived for the chemisorption of gases is:

$$\theta = K \cdot (C_{eq}) / (1 + K \cdot C_{eq}) \quad (3)$$

where,

θ : Fraction of the solid surface covered by the adsorbed molecules

K: Adsorption equilibrium constant

C_{eq} : Equilibrium concentration

Langmuir isotherm equation can be written for the gas adsorption by replacing C by P, also note that,

$$\Theta = q_{eq} / q_{eq}^m \quad (4)$$

where q_{eq}^m is the amount of adsorbate per unit mass of adsorbent required to form a monolayer.

Hence Eqn 3 takes the form of:

$$q_{eq} / q_{eq}^m = K \cdot C_{eq} / (1 + K \cdot C_{eq}) \quad (5)$$

$$C_{eq} / q = C_{eq} / q_{eq}^m + 1 / (K \cdot q_{eq}^m) \quad (6)$$

Adsorption Kinetics

When adsorption experiment takes place in a vessel with finite volume, concentration in the vessel decreases with progress of adsorption. The kinetics of adsorption can be described by several models. A pseudo second-order equation based on adsorption equilibrium capacity may be expressed in the following form;

$$\frac{dq}{dt} = k_2 (q_e - q)^2 \quad (7)$$

Where k_2 is the rate constant of pseudo second-order adsorption. Integrating and applying the initial conditions we have a linear form as;

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

The other possible model describing the adsorption kinetics is intraparticle diffusion model. The initial rate of the intraparticle diffusion is the following;

$$q = k_p \left(t^{1/2} \right) + D \quad (9)$$

Where k_p is the intraparticle diffusion rate constant $\frac{\text{mg dye}}{\text{g adsorbent min}^{1/2}}$ and D is a constant $\frac{\text{mg dye}}{\text{g adsorbent}}$ that gives idea about the thickness of the boundary layer. With diffusion rate controlling in the adsorption on particles of spherical shape the solution of the simultaneous set of differential and algebraic equations leads to;

$$F(t) = 1 - \frac{6}{\pi^2} \sum_{z=1}^{\infty} \frac{1}{z^2} \exp \left[\frac{-z^2 \pi^2 D_e t}{R_a^2} \right] \quad (10)$$

Where $F(t) = \frac{q}{q_e}$ is the fractional attainment of equilibrium at time t , D_e the effective diffusion coefficient of adsorbates in the adsorbent phase (m^2/s), R_a is the radius of the adsorbent particle assumed to be spherical (m) and z is an integer.

Fitting the eqn (10) to the whole range $0 < F(t) < 1$, for adsorption on spherical particles.

$$F(t) = \left[1 - \exp \left(\frac{-\pi^2 D_e t}{R_a^2} \right) \right]^{1/2} \quad (11)$$

This equation could be further be simplified to cover the most of the data points for calculating the effective particle diffusivity.

$$\ln \left[\frac{1}{1 - F^2(t)} \right] = \frac{\pi^2 D_e t}{R_a^2} \quad (12)$$

Thus the slope of the plot of $\ln[1/(1-F(t))]$ versus t would give D_e .

Equipment

UV Visible Spectrophotometers are used for making quantitative absorption measurements in the UV -Vis spectral region. This process finds widespread application for

the quantitative determination of a large variety of inorganic and organic species. Molecular absorption spectroscopy is based on the measurement of the transmittance or the absorbance of solutions contained in transparent cells. The concentration of an analyte in solution can be determined by measuring the absorbance at a single wavelength. The concentration of an absorbing analyte solution is linearly related to the absorbance. Wavelength scan is first performed with the reference solution and the wavelength corresponds the maximum absorbance value is found to be used to get more precise absorbance data.

Experimental Procedure

1. Prepare a standard solution of 0.012, 0.0096, 0.0048 and 0.0024 g MB / 1000 ml distilled water into the 25 ml volumetric flasks from 0.012 g MB / 1000 ml stock solution.
2. Scan the wavelength in given range to find maximum adsorbance by using UV Visible spectrophotometer.
3. Read the absorbance values for each standard solution at the determined wavelength and record the data.
4. Weigh the adsorbents
5. 5 known weight and beads of adsorbents are added to 50 ml of the MB solution having the concentration 0.012 g MB / 1000 ml.
6. Record the time of addition of methylene blue solution into the flasks, and close the surface of the flasks with stretched paper.
7. Place flasks into the shaker at 20 °C and 140 rpm.
8. Take 4 ml solution from each flask for every 20 minutes and analyze these solutions by Uv-spectrophotometer by reading the absorbance values for the determined wavelength until the equilibrium concentration is reached.
9. Record the time and data
10. Crack the adsorbent particles at the end of the experiment

Data Analysis

1. Plot the calibration curve by using absorbance data of standard solutions (concentration vs absorbance) and obtain the regression equation for calibration curve.
2. Calculate the final concentration of MB (C_{eq} , mg/L) for each sample
3. Prepare tables showing the value of q_{eq} and C_{eq} .
4. Plot adsorption isotherms of MB on Zeolite (q_{eq} vs C_{eq})
5. Apply Freundlich and Langmuir adsorption model to the experimental data and find the constants and regression coefficients.
6. Check the validity of the Freundlich and Langmuir isotherms by drawing the experimental and adsorption isotherms on the same figure.
7. Determine which one is applicable for the investigated system.
8. Draw the hypothetical figure for MB including adsorbent and solution phase for each adsorbent.
9. Plot adsorbate amount vs time for all adsorbent batches for each adsorbate types.
10. Present your adsorption kinetics results (D/R^2 , regression constants) and discuss which model well describe dye adsorption kinetics on the adsorbent.

References

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