Adsorption and its Isotherm – Theory

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Abstract : Adsorption is the process of transferring material from a fluid phase to a solid phase. The transport process involved in adsorption is analyzed by progression in complexity from batch adsorption, one-dimensional, equilibrium adsorption on a column, and one-dimensional, non-equilibrium adsorption. Adsorption is a separation process in which some materials, (adsorbate) is concentrated from a bulk vapor or liquid phase on to the surface of a porous solid (adsorbent). Some common examples of adsorption are the, silica gel packets to adsorb moisture from packaged electronic or optical equipment, and carbon "filter" to deodorize drinking water.

Keywords: Adsorption, Adsorbate, Adsorbate, Carbon Filter.

I. Introduction:

Preferential concentration of one component of a system at an interface, where the local concentration is different from those in the bulk phase. positive adsorption is the interfacial concentration of the adsorbed species is greater than that in the bulk phase whereas decrease the interfacial energy. Negative adsorption is th increase the interfacial energy of a system. Two aspects that can be addressed in consideration of adsorption processes are Thermodynamics which is the final equilibrium interfacial energy and second Kinetics which is the rate at which the adsorption process occurs.

The fundamental concept in adsorption is the adsorption isotherm. It is the equilibrium relation between the pressure or concentration in the bulk fluid phase at constant temperature and quantity of the adsorbed. The original Gibbs treatment, that is appropriate for fluid interface, the real interface is assumed to be a geometrical plane called the Gibbs dividing surface GDS .The Gibbs approach has no model and a formal character is required of structure of the interface layer.

Mechanism of Adsorption:
Adsorbate: The substance that concentrates at the surface is called adsorbate.
Adsorbent: The material upon whose surface the adsorption takes place is called an adsorbent. Mostly activated carbon is used as an adsorbent. Adsorbents are used in the form of rods, moldings, spherical pellets, or monoliths diameters between 0.5 and 10 mm. They may have high abrasion resistance, small pore diameters and high thermal stability, which results in higher exposed surface area and hence high surface capacity for adsorption. The adsorbents should also have a pore structure which helps in fast transport of the gaseous vapors.
The adsorbents categorized into one of three classes:
1. Oxygen-containing compounds are typically hydrophilic and polar, including materials such as silica gel and zeolites.
2. Compounds of carbon-based are typically nonpolar, and hydrophobic including materials such as activated carbon and graphite.
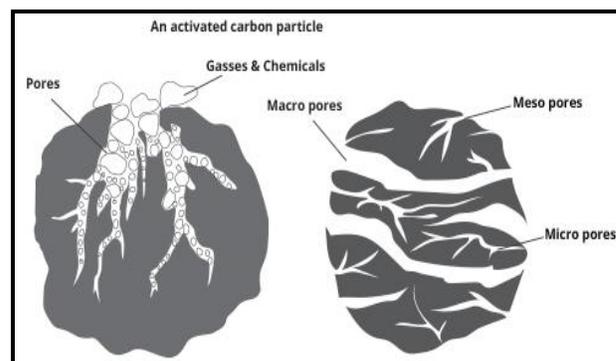3. Polymer-based compounds are polar or non-polar functional groups in a porous polymer matrix.

Figure No-1: Showing Mechanism of adsorption[i]

Adsorption Principles
The basic principle of operation for carbon adsorption is the mass transfer and adsorption of a molecule from a liquid or gas into solid surface. Activated carbon is manufactured in such a way as to

produce extremely porous carbon particles whose internal surface area is very large .This porous structure attracts and holds organic molecules, inorganic molecules. as well as metals.
Adsorption occurs because
i) The contaminant has low solubility in the waste
ii) The contaminant has greater affinity for the carbon than for the waste
iii) A combination of two
The Two most commonly used carbon adsorption processes are the granular activated carbon (GAC) which is used in packed beds, and the powdered activated carbon. The activated carbon adsorption process is one of the most applied technologies for the removal of trace organic compounds from an aqueous solution. Activated carbon ratio should be in the range of 500 to 1000 m^2/g which is a good adsorbent for effective removal of organic compounds.

II. **Material and Methodology**:
Batch Flow System: In batch type contact operation, some quantity of carbon is continuously mixed with a specific volume of wastewater until the pollutant in that solution has been decreased to a desired level. The carbon is then removed and is discarded or regenerated for use. These processes are usually limited to the treatment of small volume of effluents.
Column Flow System: These operation appears to have various advantages over batch operation, because rates of adsorption depend on the concentration of the solute in solution being treated. For Column operation, the carbon is continuously kept in contact with a fresh solution. Solid adsorbent may be added at the top of the column and spent adsorbent drained from the bottom.
There are 3 types of continuous flow systems namely. Fixed Bed Adsorption system Fluidized Bed Adsorption System Moving Beds (or) Expanded Bed Adsorption system. Fixed bed Adsorption System is used to treat large quantities of wastewater in fixed bed adsorption system, the flow could be either down flow or up flow, packed bed up flow carbon columns for full counter current operation are suitable only for low turbidity water (i.e.) water having a turbidity of 2.5 JTU. The advantage of this is the reduction capital cost. The down flow bed may be fixed either in series or in parallel. Many designs consist of either two to three beds in series.

When the adsorptive capacity of the solid is reached, it is regenerated for reuse. In liquid down flow operation, the entire contents of the column are regenerated after exhaustion.

III. **Results and Tables:**
Adsorption Isotherm:
Adsorption process is studied through graphs known as adsorption isotherm. Adsorption is the adsorbate on the adsorbent as a function if its pressure or concentration at constant temperature .The quantity adsorbed is nearly always normalized by the mass of the adsorbent. From the above we can predict that after saturation pressure Ps, adsorption does not occur anymore, that is there are limited numbers of vacancies on the surface of the adsorbent. At high pressure a stage is reached when all the sites are occupied and further increase in pressure does not cause any difference in adsorption process. At high pressure, adsorption is independent of pressure.
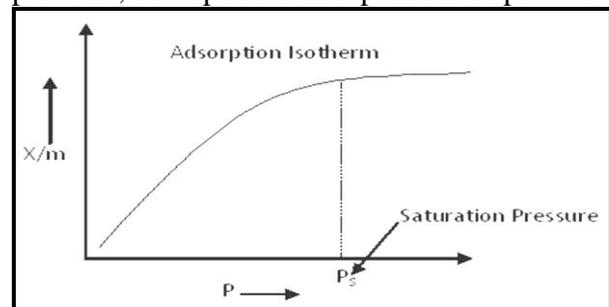

Figure No-2: Showing Adsorption Isotherm

Types of Adsorption Isotherm
 Type I adsorption isotherm
The above graph shows Monolayer adsorption. This graph can be explained using Langmuir Adsorption Isotherm. Some Examples of Type-I adsorption are Adsorption of Nitrogen (N2) or Hydrogen (H) on charcoal at temperature near to -1800°C.
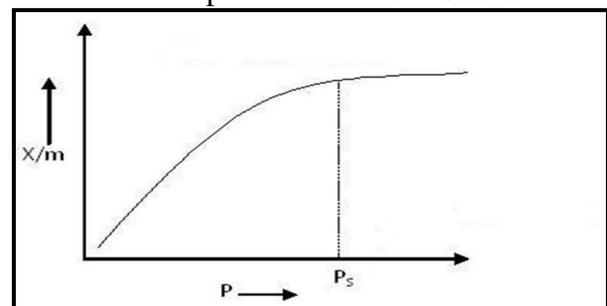

Figure No 3: Showing Type I Adsorption Isothem
Type II Adsorption Isotherm

Type II Adsorption Isotherm shows huge deviation from Langmuir model of adsorption. monolayer formation takes place due to the intermediate flat region in the isotherm. Examples of Type-II adsorption are Nitrogen (N_2 (g)) adsorbed at- 1950°C on silica gel and Nitrogen (N2 (g)) adsorbed at - 1950°C on Iron(Fe) catalyst
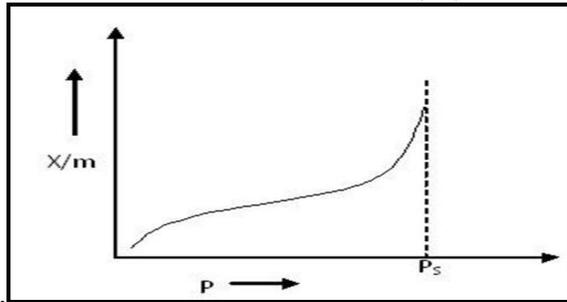

Figure No 4: Showing Type II Adsorption Isotherm

Type III Adsorption Isotherm
At lower pressure the region of graph is quite similar to Type II. Thus this explains formation of monolayer followed by multilayer. The intermediate flat region in the isotherm corresponds to monolayer formation. The saturation level reaches at a pressure below the saturation vapor pressure. This can be explained on the basis of a possibility of gases getting condensed in the tiny capillary pores of adsorbent at pressure below the saturation
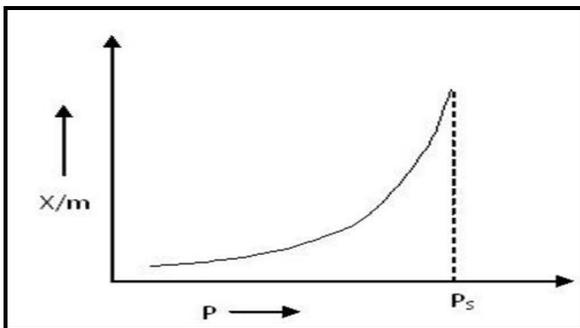

Figure No-5: Showing Type III Adsorption Isotherm

Type IV Adsorption Isotherm
At lower pressure region of graph is quite similar to Type II. This explains formation of monolayer followed by multilayer. The intermediate flat region in the isotherm corresponds to monolayer formation. The saturation level reaches at a pressure below the saturation pressure (Ps) of the gas. Example of Type IV adsorption isotherm is adsorption of Benzene on

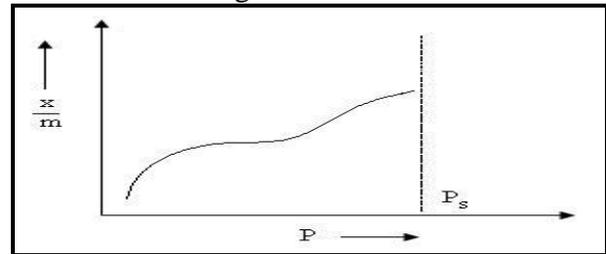Iron oxide at 500oC and adsorption of Benzene on Silica gel at 500oC.

Figure No-6: Showing Type IV Adsorption Isotherm

Type V Adsorption Isotherm
Explanation of Type V graph is similar to Type IV. Example of Type V Adsorption Isotherm is adsorption of Water (vapors) at 1000°C on charcoal.[ii]
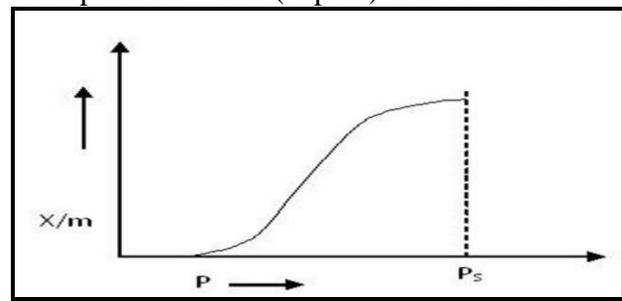

Figure No-7: Showing Type V Adsorption Isotherm

Freundlich Isotherm: The Freundlich adsorption isotherm is an adsorption isotherm, which is a curve relating the concentration of a solute on the surface of an adsorbent, with the concentration of the solute in the liquid with which it is in contact. In 1909, he gave an empirical expression representing the isothermal variation of Adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure. This equation is known as Freundlich Adsorption Isotherm or Freundlich Adsorption equation.
The Freundlich Adsorption Isotherm is mathematically expressed as

$$x/m = Kp^{1/n}$$
$$\log (x/m) = \log K + (1/n) \log p$$
or
$$x/m = K c^{1/n}$$
It is also written as
$$\log (x/m) = \log K + (1/n) \log c$$

Where,
x = mass of adsorbate
m = mass of adsorbent

p = Equilibrium pressure of adsorbate

c = Equilibrium concentration of adsorbate in solution.

K and n are constants for a given adsorbate and adsorbent at a particular temperature. At high pressure $1/n = 0$ Hence extent of adsorption is independent of pressure but at high pressure it is adsorbate between the surface and the gas phase. The basic limitation of Langmuir adsorption equation is that it is valid at low pressure only. At lower pressure, KP is so small, that factor (1+KP) in denominator can almost be ignored. So Langmuir equation reduces to denominator is nearly equal to KP. So Langmuir equation reduces to

$$0=KP/1+KP$$
$$0=KP$$

based on four assumptions: i) The surface of the adsorbent is uniform, that is, all the adsorption sites are equivalent. ii) Adsorbed molecules do not interact. iii) All adsorption occurs through the same mechanism. iv) At the maximum adsorption, only a

IV. CONCLUSION

Adsorption science has a very long history, and its first practical adoptions were noted in ancient times. The current adsorption theory and relevant applications initiated by Langmuir's fundamental work have been developed extensively during the last 80 years. Presently, they comprise very advanced approaches that include a wide spectrum of modern surface chemistry. The autonomous existence of adsorption science is due to two unquestionable facts: the enormous complexity that is inherent to adsorption phenomena at various interfaces, and the widespread, general occurrence of great practical importance. Nowadays, only such technologies which give the possibility of sustainable development of people and society are

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A0wDQ&iact=mrc&uact=8

dependent on pressure. There are some limitations of Freundlich adsorption isotherm. Experimentally it

Langmuir Isotherm:

In 1916, Irving Langmuir published a new model isotherm for gases adsorbed to solids, which retained his name. It is a semi-empirical isotherm derived from a proposed kinetic mechanism. It is monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent. Based on his theory, Langmuir derived an equation which explained the relationship between the number of active sites of the surface undergoing adsorption and pressure. This equation is called Langmuir equation.[iv]

$$0= KP/1+KP$$

where,

0- the number of sites of the surface which are covered with gaseous molecule,

P - pressure

K - is the equilibrium constant for distribution of and importance of adsorption and related domains in nature, including everyday life's products, industrial and environmental applications.

It is widely known, that broadly-understood adsorption science has gained a dominating role in modern industry under environmental, economical and energy saving aspects. Doubtless, adsorption technologies are rapidly improved and adopted to contemporary tasks of mankind. Both industrial as well as recent environmental problems require wide body scientists and engineers to develop the theory of adsorption science and to produce new adsorbents, catalysts and other advanced solids

justified. Adsorption, catalysis and aforementioned related fields have a major impact on development in many areas central to the question of our future.[iv]
ii.

http://shodhganga.inflibnet.ac.in/bitstream/10603/22665/8/08_chapter
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iii.   http://www.che.ncku.edu.tw/facultyweb/leeyl/94%20%E7%
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Chemistry, M.Curie-Skłodowska University,20031Lublin,Poland.
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0Theory%20to%20practice_Dabrowski.pdf