Extraction, Leaching, Adsorption Concepts and Equipments

Separation processes - general

▶ Mechanical separations e.g. filtration of a solid from a suspension in a liquid, centrifugation, screening etc

▶ Mass transfer operations e.g. distillation, extraction etc

Mass transfer operations – nature of interface between phases:

▶ Gas-liquid contact e.g. absorption, evaporation, distillation etc

▶ Liquid-liquid contact e.g. extraction

▶ Liquid-solid contact e.g. crystallization, adsorption

▶ Gas-solid contact e.g. adsorption, drying etc

Hierarchy of Separation Technologies

Physical Separations
Decantation, Coalescing, Filtration, Demisting

Evaporation
Single Effect, Multiple Effect

Distillation
Simple, Azeotropic, Extractive, Reactive

Extraction
Simple, Fractional, Reactive

Adsorption
Pressure Swing, Temperature Swing

Crystallization
Melt, Solvent

Membranes
MF, UF, NF, RO

Easy

Difficulty Of Separation

Difficult

Liquid-liquid extraction :

It is a useful method to separate components (compounds) of a mixture

Mixture

Separated
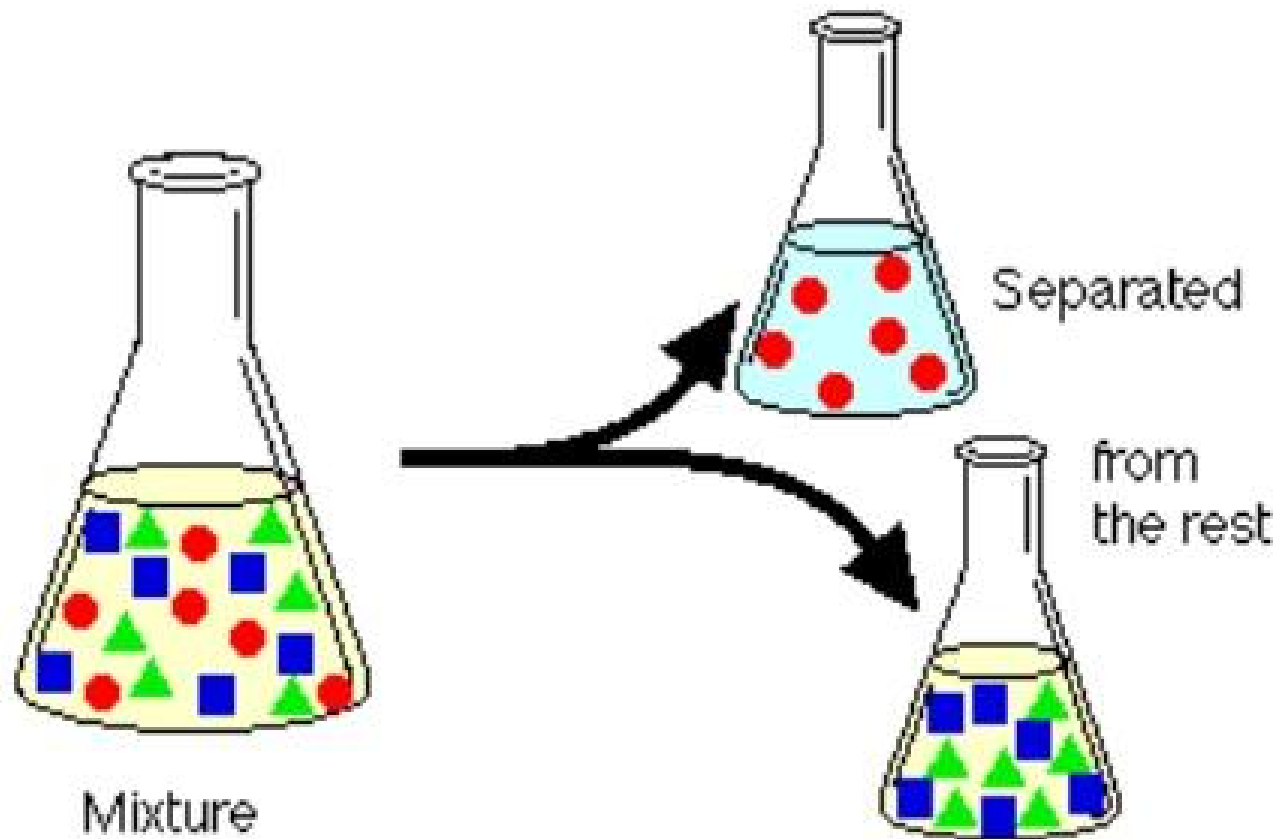
from
the rest

Let's see an example.

Suppose that you have a mixture of **sugar** in **vegetable oil** (it tastes sweet!) and you want to **separate the sugar from the oil**. You observe that the sugar particles are too tiny to filter and you suspect that the sugar is partially dissolved in the vegetable oil.

Vegetable oil and sugar

Tastes so sweet...
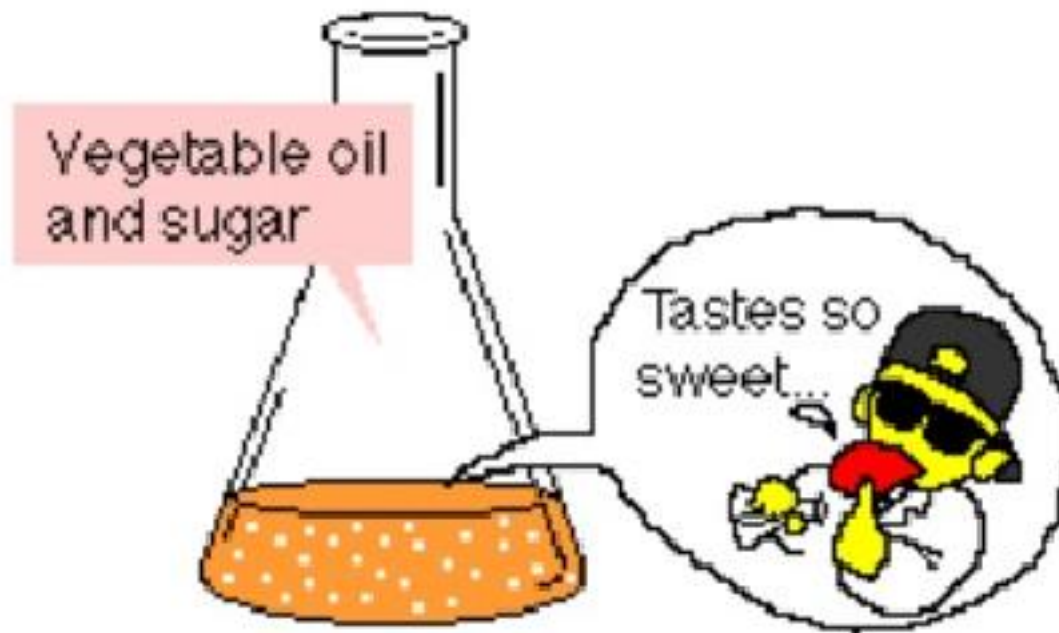
How about **shaking the mixture with water**

Will it separate the sugar from the oil? **Sugar is much more soluble in water than in vegetable oil**, and, as you know, water is *immiscible* (=not soluble) with oil.


Did you see the result? The **water phase is the bottom layer** and the **oil phase is the top layer**, because **water is *denser* than oil**.

*You have not shaken the mixture yet, so sugar is still in the oil phase.
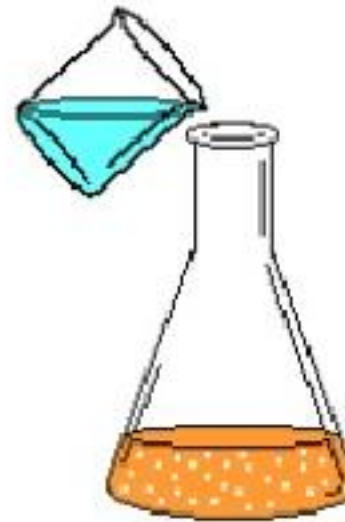
By shaking the layers (phases) well, you increase the contact area between the two phases. The **sugar will move to the phase in which it is most soluble: the water layer**

Now the water phase tastes sweet, because the sugar is moved to the water phase upon shaking.**You extracted sugar from the oil with water**.**In this example, water was the extraction solvent ;the original oil-sugar mixture was the solution to be extracted; and sugar was the compound extracted from one phase to another. Separating the two layers accomplishes the separation of the sugar from the vegetable oil
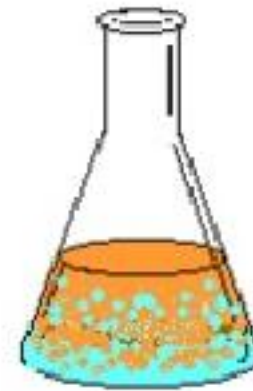
Oil Phase

Water phase

Now the water layer tastes sweet...

Did you get it? .....the concept of liquid-liquid extraction?

Liquid-liquid extraction is based on the transfer of a solute substance from one liquid phase into another liquid phase according to the solubility. Extraction becomes a very useful tool if you choose a suitable extraction solvent.You can use extraction to separate a substance selectively from a mixture, or to remove unwanted impurities from a solution. In the practical use, usually one phase is a water or water-based (aqueous) solution and the other an organic solvent which is immiscible with water.

The success of this method depends upon the difference in solubility of a compound in various solvents. For a given compound, solubility differences between solvents is quantified as the "**distribution coefficient**"

Basic principles

In liquid-liquid extraction, a soluble component (the solute) moves from one liquid phase to another. The two liquid phases must be either immiscible, or partially miscible.

➢ usually isothermal and isobaric

➢ can be done at low temperature (good for thermally fragile solutes, such as large organic molecules or biomolecules)

➢ can be very difficult to achieve good contact between poorly miscible liquids (low stage efficiency)

➢ extracting solvent is usually recycled, often by distillation (expensive and energy-intensive)

➢ can be single stage (mixer-settler) or multistage (cascade)

Example - Penicillin G

6-aminopenicillanic acid (6-APA) is
manufactured by GSK in Irvine. It is used to
manufacture amoxicillin and 'Augmentin'.

Fermentation products (penicillin G broth) are
filtered (microfiltration) and extracted at low
pH with amyl acetate or methyl isobutyl
ketone. The penicillin G is then extracted
further at a higher pH into an aqueous
phosphate buffer.

Choice of solvent

Factors to be considered:

- Selectivity
- Distribution coefficient
- Insolubility of solvent
- Recoverability of solute from solvent
- Density difference between liquid phases
- Interfacial tension
- Chemical reactivity
- Cost
- Viscosity, vapour pressure
- Flammability, toxicity

Selectivity:

$$\beta = \frac{\text{(mass fraction B in E)/(mass fraction A in E)}}{\text{(mass fraction B in R)/(mass fraction A in R)}}$$

$\beta > 1$

Distribution coefficient:

$K = y/x$

Large values are desirable since less solvent is required for a given degree of extraction

Physical properties:

► Low viscosity

► Low vapour pressure

► Non-flammable (high flash point)

► Non-toxic

Recoverability of solvent and solute:

▶ No azeotrope formed between solvent and solute

▶ Mixtures should have a high relative volatility

▶ Solvent should have a small latent heat of vaporization

Density:

➢ A density difference is required between the two phases.

Interfacial tension:

The larger the interfacial tension between the two phases the more readily coalescence of emulsions will occur to give two distinct liquid phases but the more difficult will be the dispersion of one liquid in the other to give efficient solute extraction.
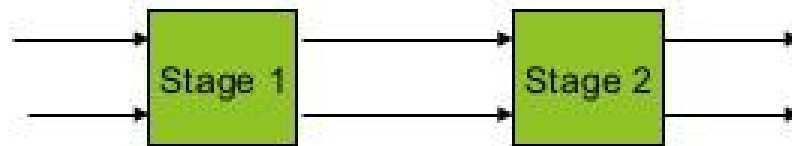
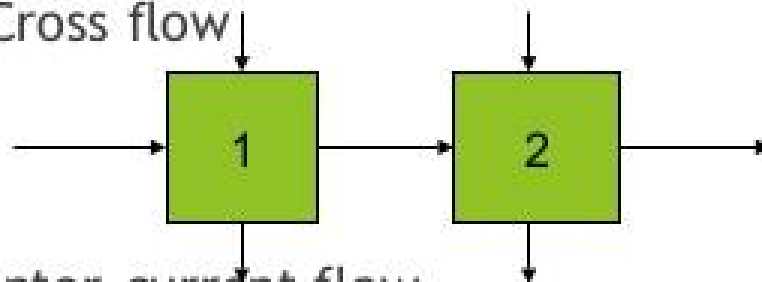## Chemical reactivity:

Solvent should be stable and inert.
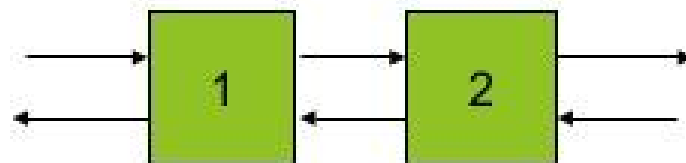
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Types of flow in LLE

When both phases are flowing:

▶ Co-current contact

▶ Cross flow

Counter-current flow

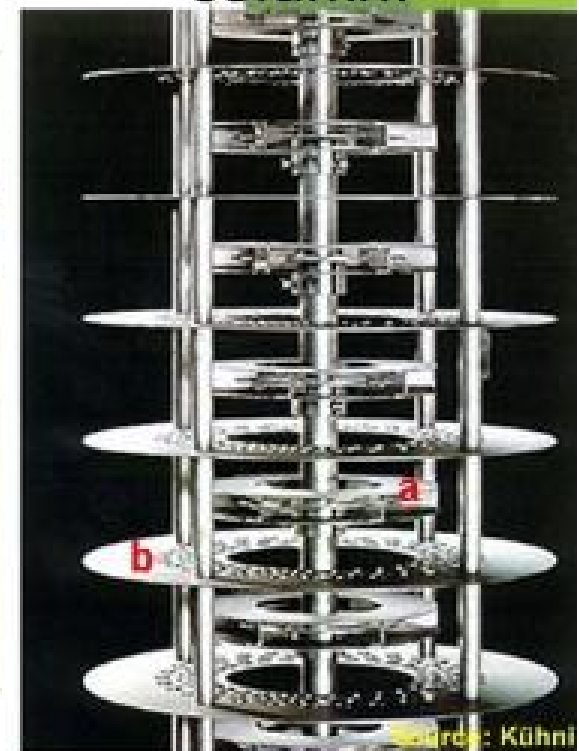# Extraction equipment

Batch:

separatory funnel

Continuous:

single-stage:

mixer-settler

column:

Source: Kühni

rotating-disk contacter
a. agitator; b. stator disk

Typical Applications

- Remove products and pollutants from dilute aqueous streams

- Wash polar compounds or acids/bases from organic streams

- Heat sensitive products

- Non-volatile materials

- Azeotropic and close boiling mixtures

- Alternative to high cost distillations

Extraction is Used in a Wide Variety of Industries

Chemical
- Washing of acids/bases, polar compounds from organics

Pharmaceuticals
- Recovery of active materials from fermentation broths
- Purification of vitamin products

Effluent Treatment
- Recovery of phenol, DMF, DMAC
- Recovery of acetic acid from dilute solutions

Polymer Processing
- Recovery of caprolactam for nylon manufacture
- Separation of catalyst from reaction products

Petroleum
- Lube oil quality improvement
- Separation of aromatics/aliphatics (BTX)

Petrochemicals
- Separation of olefins/parafins
- Separation of structural isomers

Food Industry
- Decaffeination of coffee and tea
- Separation of essential oils (flavors and fragrances)

Metals Industry
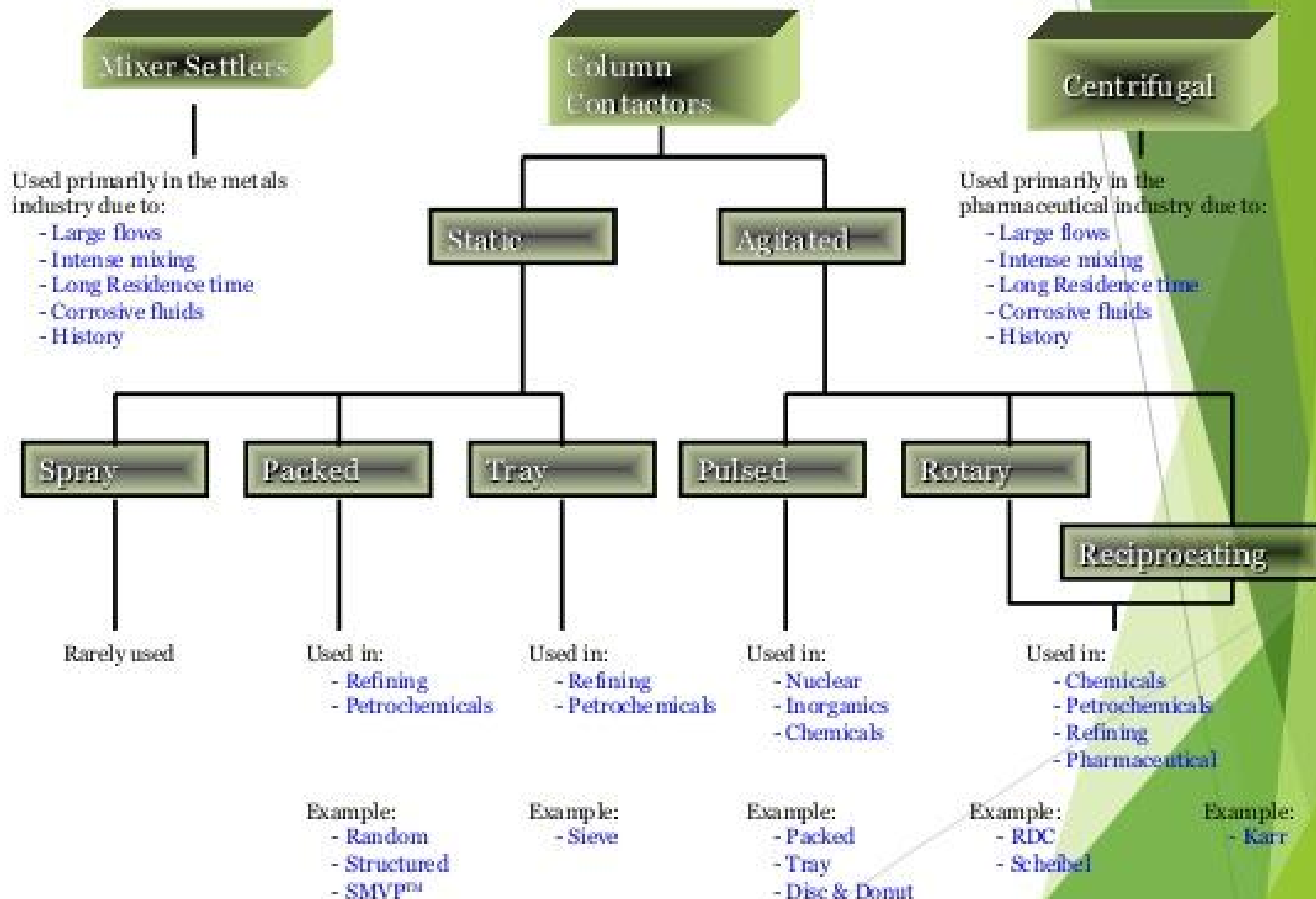- Copper production
- Recovery of rare earth elements

Inorganic Chemicals
- Purification of phosphoric acid

Nuclear Industry
- Purification of uranium

Major Types of Extraction Equipment

Mixer Settlers

Used primarily in the metals industry due to:
- Large flows
- Intense mixing
- Long Residence time
- Corrosive fluids
- History

Column Contactors

Static

Agitated

Centrifugal

Used primarily in the pharmaceutical industry due to:
- Large flows
- Intense mixing
- Long Residence time
- Corrosive fluids
- History

Spray

Rarely used

Packed

Used in:
- Refining
- Petrochemicals

Example:
- Random
- Structured
- SMVP™

Tray

Used in:
- Refining
- Petrochemicals

Example:
- Sieve

Pulsed

Used in:
- Nuclear
- Inorganics
- Chemicals

Example:
- Packed
- Tray
- Disc & Donut

Rotary

Used in:
- Chemicals
- Petrochemicals
- Refining
- Pharmaceutical

Example:
- RDC
- Scheibel

Reciprocating

Example:
- Karr

:EXTRACTORS

Liquid-liquid extraction has only become popular as a separations technique in the past thirty years. In this time, liquid-liquid extractors have become the separation   equipment of choice for selected processes.

# ROTATING DISC LIQUID-LIQUID)5 :EXTRACTION UNIT

HIS Rotating Disc Liquid-Liquid Extraction Unit has been designed to demonstrate the

basic principles of a liquid-liquid extraction process. When separation by distillation is ineffective or very

difficult, liquid-liquid extraction is one of the main alternatives to consider. Close boiling mixtures or substances

that cannot withstand the temperature of distillation, even under a vacuum, may often be separated from impurities by

extraction, which utilizes chemical differences instead of vapor .pressure differences

Separation by liquid-liquid extraction can be defined as the selective removal of one or more components either

from a homogeneous liquid mixture or from a solution, using a second liquid or solvent, which is partially or wholly .immiscible with the first

:EXTRACTION UNIT

The normal mode of operation is that the light phase and heavy phase liquids are pumped counter currently into the extraction column. The heavy phase will enter the top of the column and flow downwards while the light phase will enter the bottom of the column and flow upwards due to density differences. Countercurrent flow in the column and agitation of the two phases by the rotating disc will cause the transfer of solute component from one phase (raffinate) to the other (extract). The raffinate will emerge at the bottom while the extract will emerge at the top of the extraction column. This liquid liquid extraction process is done in numerous continuous stages throughout the column to give a higher degree of separation.

Liquid – liquid extraction
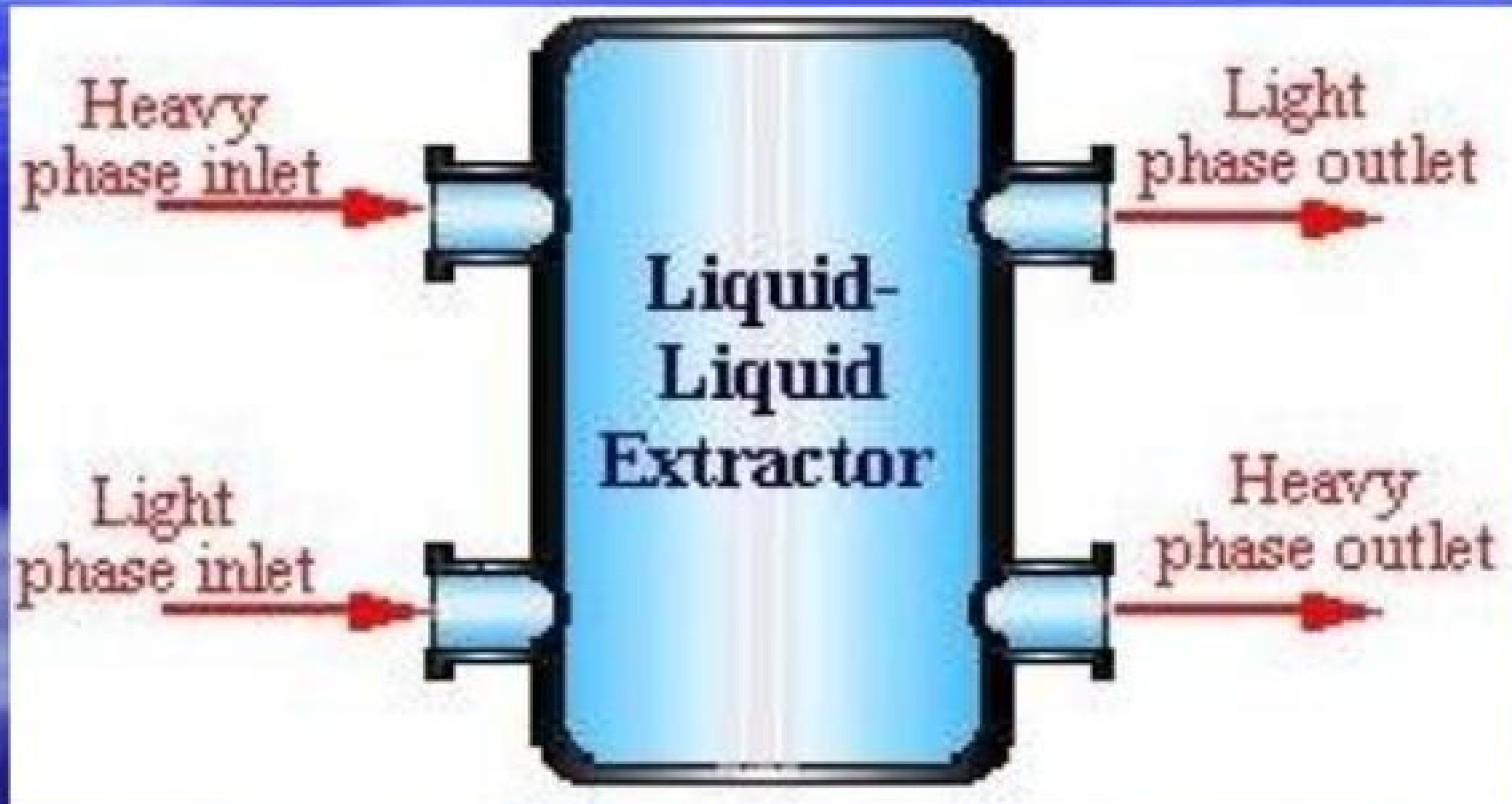
:GENERAL INFORMATION

- Mixer-settler liquid-liquid extractors have two stages. In the mixing stage the immiscible solvent and the solute-carrying feed are brought into contact, droplets are formed by mixing, and the desired solute(s) are extracted by the solvent. To learn more about different mixer designs see the *Mixers* section of this encyclopedia.

- In the settler the two liquid components do just that, they settle out into two phases. The heavier phase exits out the bottom of the settler and the lighter phase is drawn off the top. To learn more about different settler designs see the *Gravity Separators* section of this encyclopedia.

:EQUIPMENT DESIGN

For most processes one mixer and one settler will not be enough to achieve effective separation. Often a system is designed with several mixer-settler stages in series. Although the flow of the two liquid phases can be *countercurrent, cocurrent* or *cross flow*, solvent use is most inefficient in cross flow. The transportation of the liquids from one stage to the next occurs either by gravity or using pumps. The schematic below shows a countercurrent system with three mixers and settlers in series.

:USAGE EXAMPLES

The mixer-settler system shown here is used in chemical processing. Mixer-settler systems, became quite popular in the metals industry for their ability to handle high throughputs that required long residence times. They have grown to find much use in several other processes, such as aromatic extraction and nuclear fuel processing. Shown below to the left is an example of a stainless steel 3-stage mixer-settler liquid extractor. To the right is an example of a mixer-settler with a tubular design used for glass, enamelled steel and other metallic materials with high operational pressures.
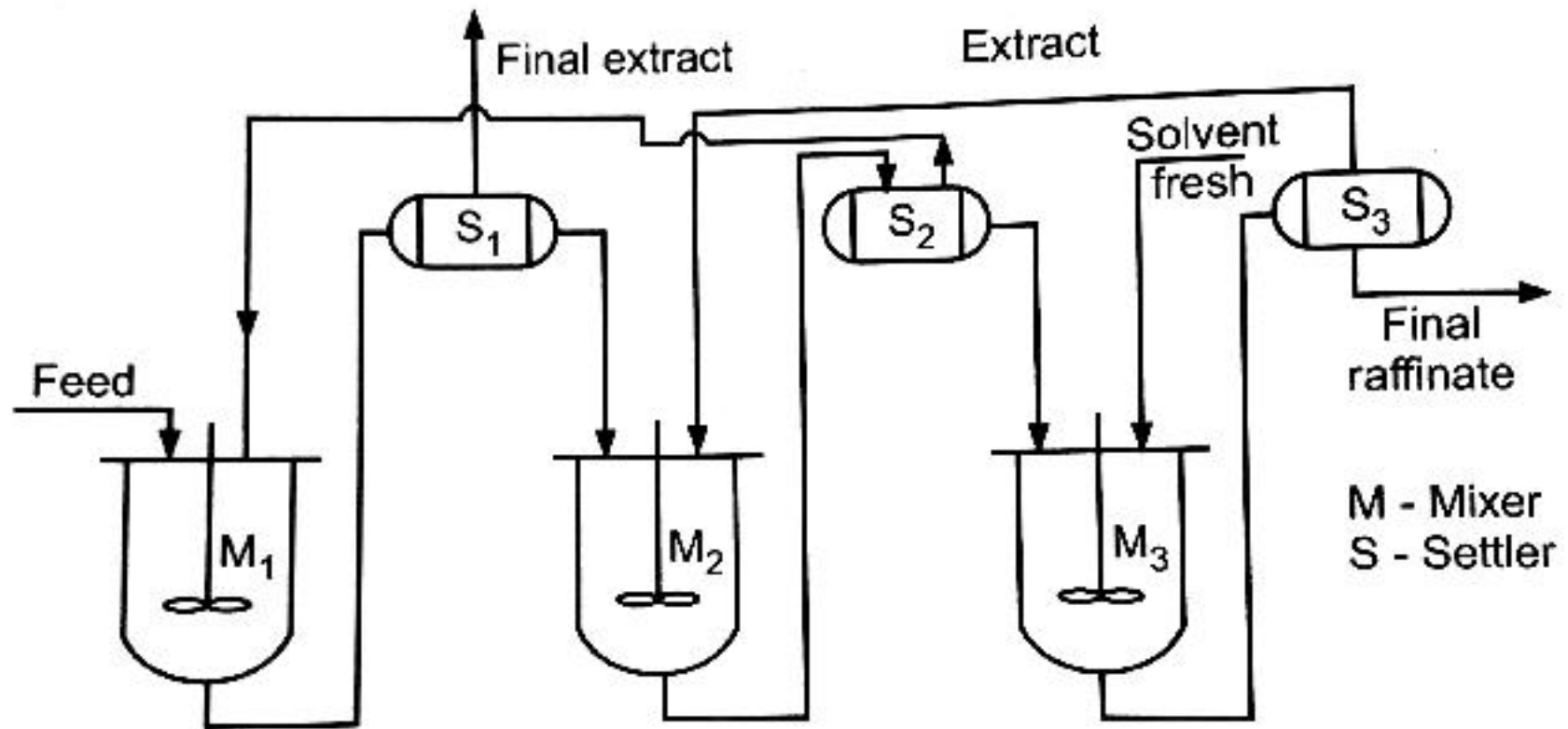
:Examples

ADVANTAGES

.Reliable scale up techniques

.Can handle high flow rates

.Ideal for processes with slow mass transfer

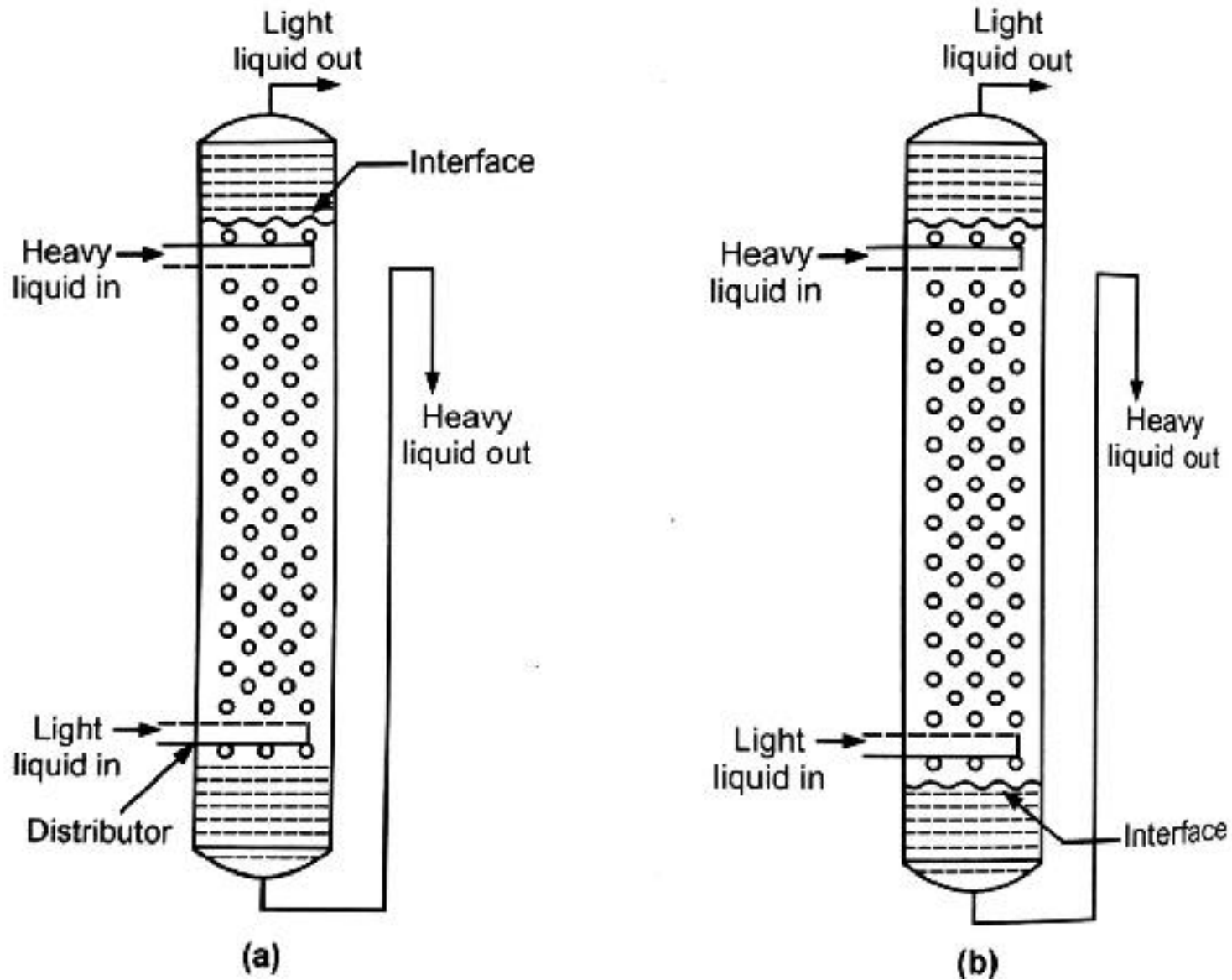Intense mixing, resulting in small droplets for good mass transfer

Batch Mixer Settler
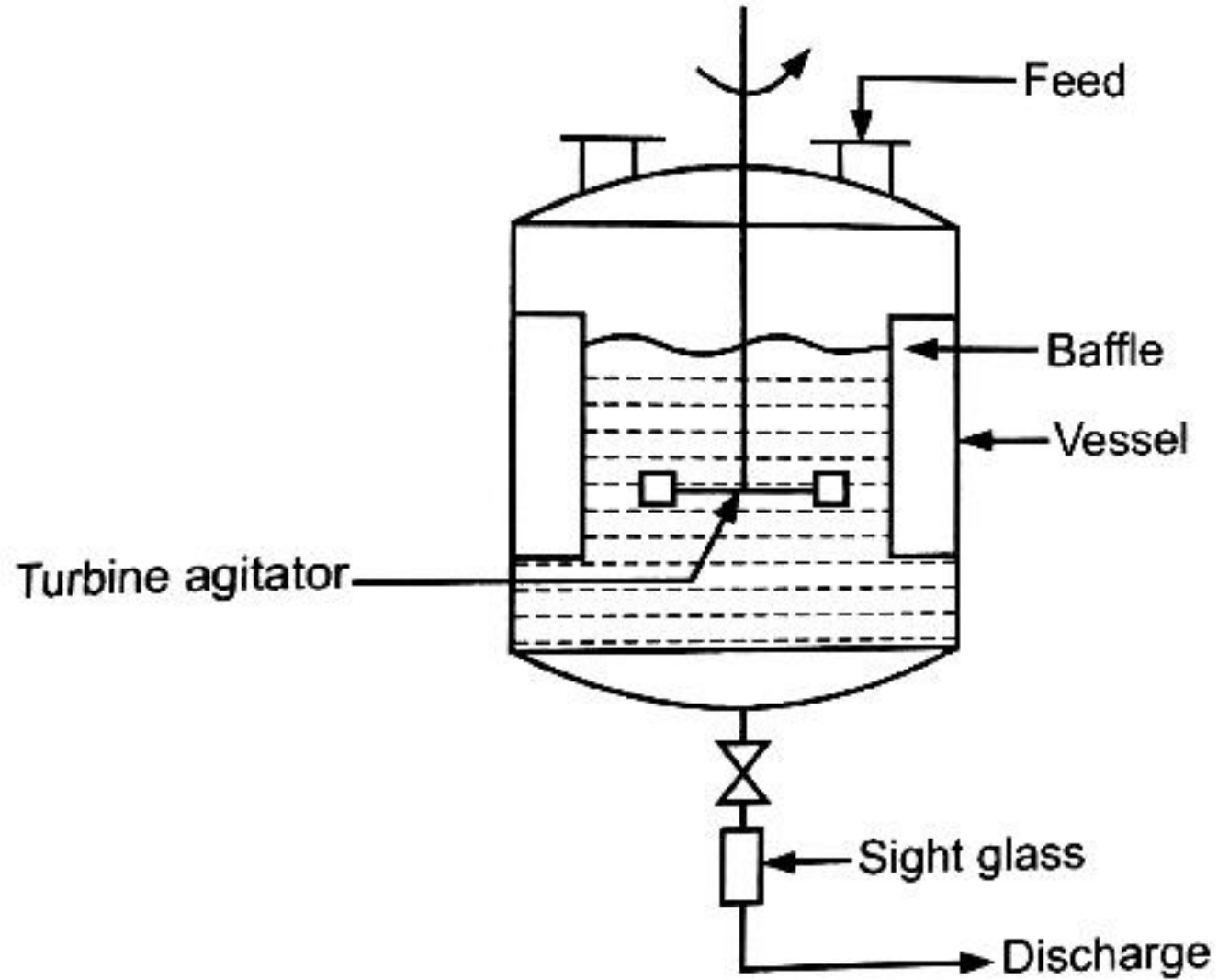
Continuous Mixer Settler

# Spray Tower

(a)   (b)

:Spray Column) 2

This set-up merely consists of an empty shell with provisions at the end for introducing and removing the liquids. Its construction is the simplest but suffers from low efficiency due to poor phase contacting and excessive back-mixing in the continuous phase. Because of their simple construction, spray columns are still used in the industry for simple operations such as washing and neutralization.

SPRAY - COLUMNS

Spray column liquid-liquid extractors are the simplest of the column designs. The dispersed phase is introduced via a nozzle either at the top or the bottom of the column, depending on whether the heavy phase or light phase is being dispersed. The continuous phase enters the opposite end of the column, resulting in mass transfer through the vertical counter flow of the two phases. There is no dispersion-coalescence cycle inside the column, resulting in very low efficiency for spray columns. Spray columns work best for fluids containing large suspended solids.

Packed Tower
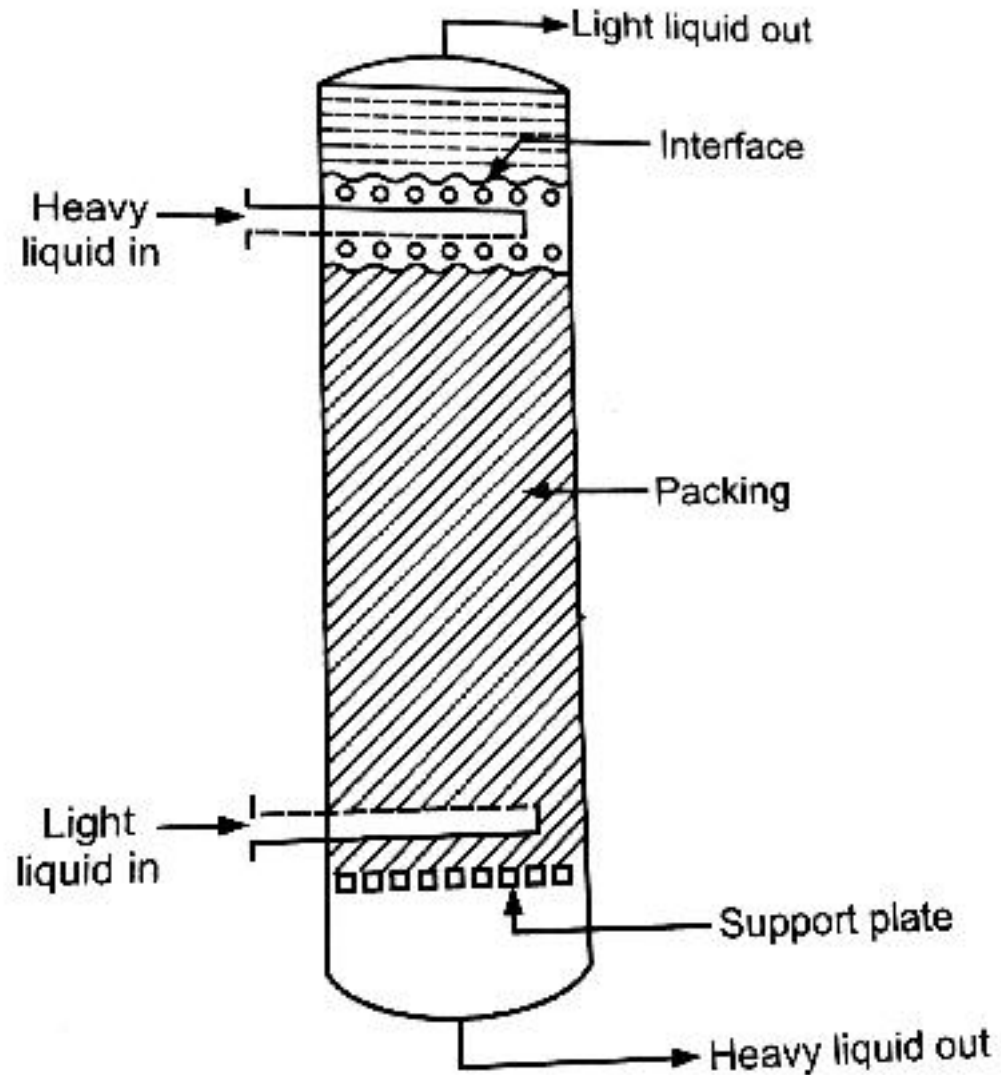
3(Packed column:

liquid-liquid extractors are also similar to those seen in other separations sections of this encyclopedia. The packing, which assists in droplet formation, can either be structured in a mesh net or randomly placed in the column. Dispersion is accomplished with a nozzle at the top or bottom of the column, depending on whether the heavy or the light phase is being dispersed. As in sieve tray columns, the internals of the column need to be coated with the continuous phase.

PACKED – COLUMN

Light phase out

Heavy phase in

Interface

Dispersion unit

Light phase in

Heavy phase out
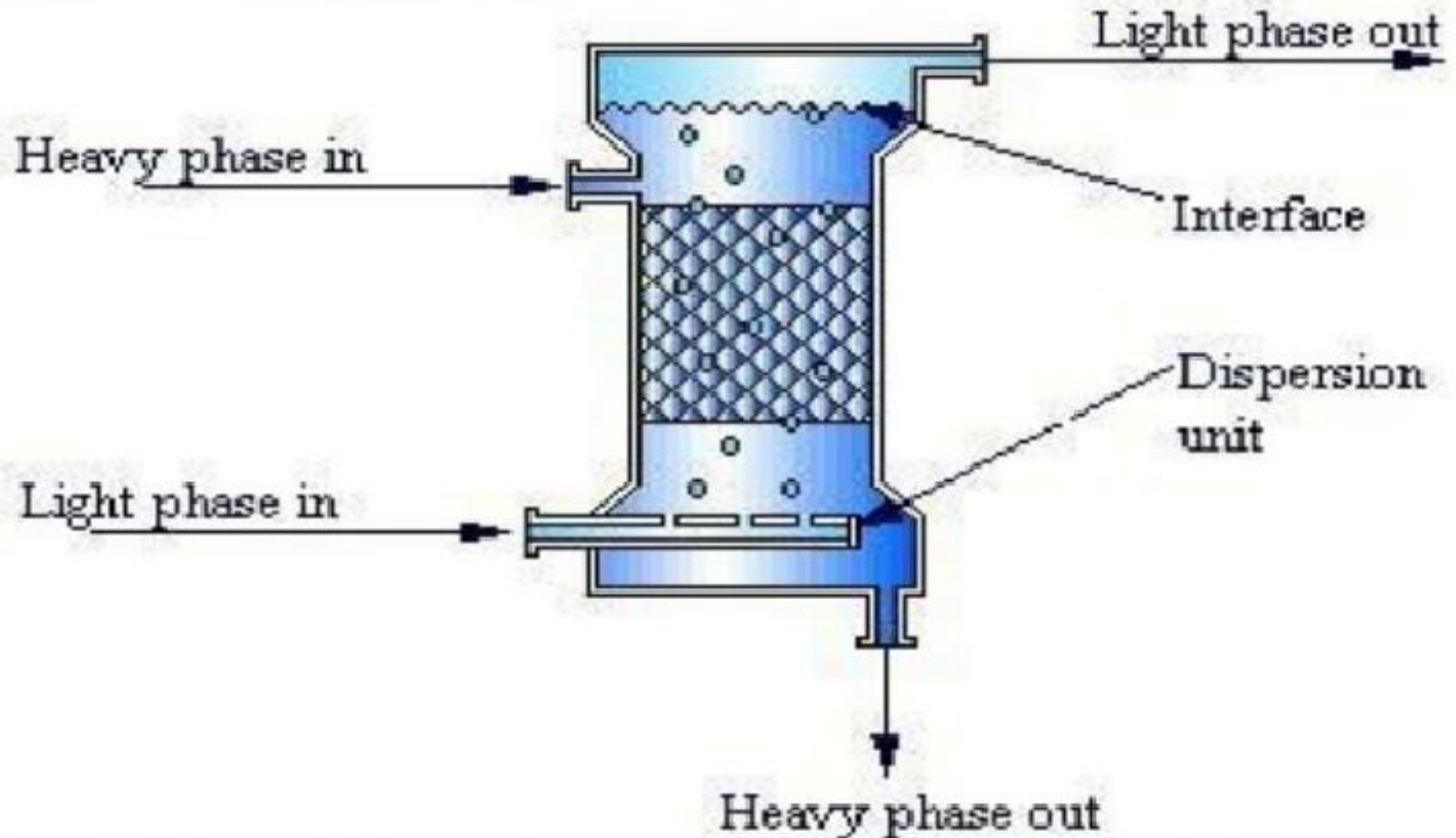
ADVANTAGES

- .Spray columns are inexpensive

- Sieve tray columns can handle a very sizeable .throughput

- Sieve tray columns have had good success .with scale up procedures

- Packed columns are highly efficient when only .a few stages are needed

DISADVANTAGES

- Spray columns are very inefficient.
- Sieve tray and packed columns can suffer from solids plugging.
- Packed columns have lower throughput due to the packing.
- Packed columns are hard to scale up accurately.
- The initial dispersion is a concern packed columns, to avoid channeling
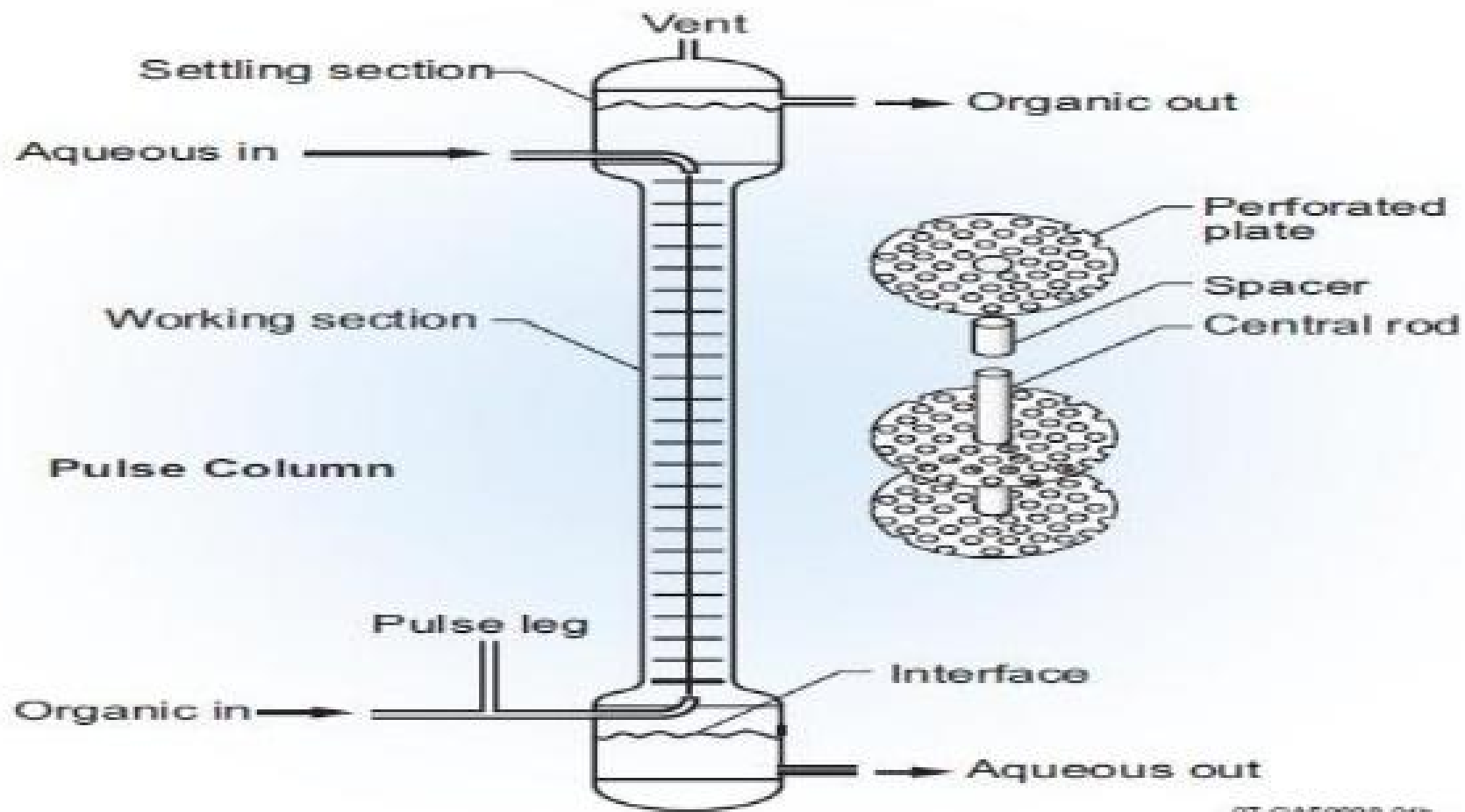
Rotating Disc or Agitated Tower
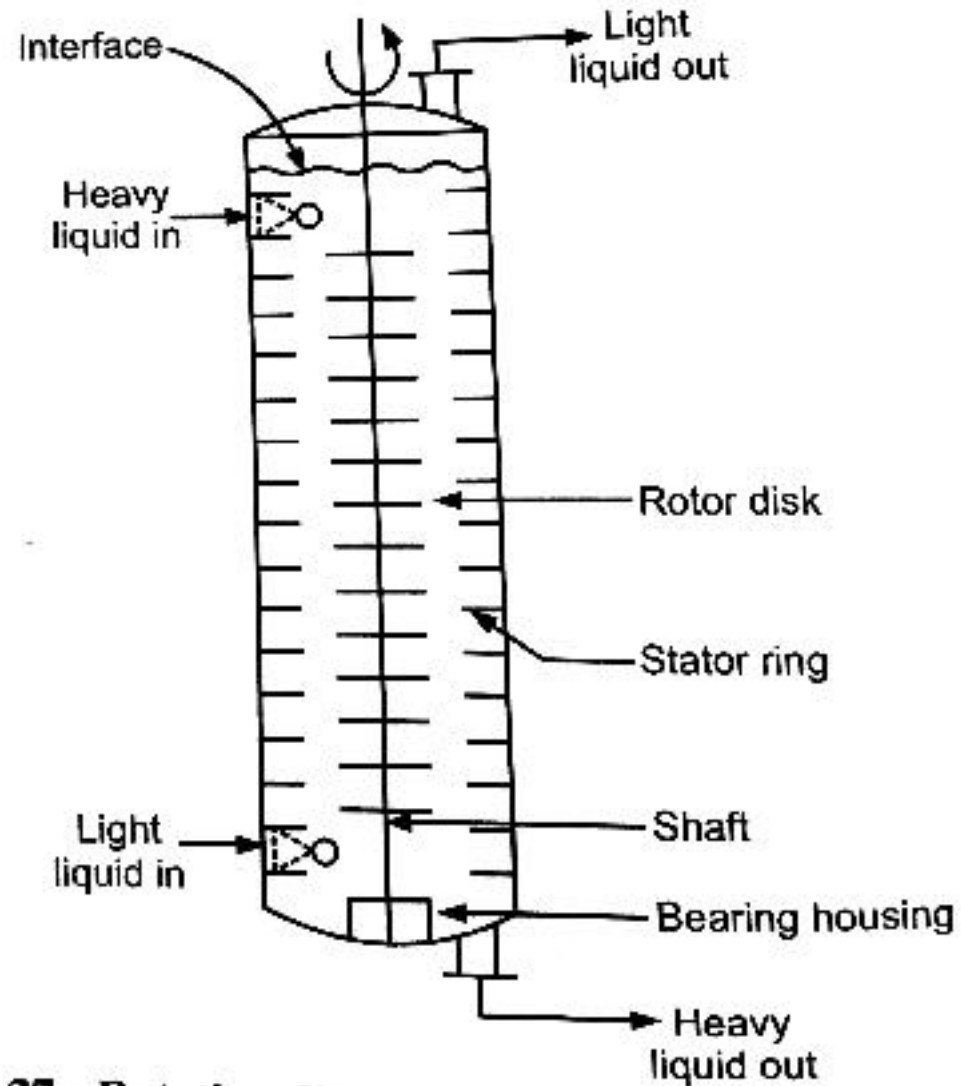
Figure 4. Pulse Column with perforated plates

- **The Pulse Extraction Process** (P.E.P.) developed by JURA optimise the extraction time.

- It forces the hot water through the ground coffee at short intervals.

- This process allows the flavours of the coffee to fully develop.

DISADVANTAGES

Packing in packed column hinders flow

More expensive than non-agitated columns

ADVANTAGES

Increases efficiency two fold

No internal mechanical parts makes repairs easy

Unit-III: Leaching

Leaching

- Leaching is a preferential solution of one or more constituents of solid mixture by contact with a liquid solvent. This unit operation is one of the oldest in the chemical industries.

Industrial application

- Leaching is widely used in the biological and food processing industries, such as the separation of sugar from sugar beets with hot water.

- The extraction of oils from peanuts, soybeans, sunflower seeds, cotton seeds, and halibut livers.

- In pharmaceutical industry, many products are obtained by leaching plant roots, leaves, and stems.

- In the metals processing industry, leaching is used to remove the metals from their ores, which contains many undesirable constituents, as solute salts.

- In gold leaching, gold is leached from its ore using an aqueous sodium cyanide solution.

Leaching equipments

- Agitated vessels
- Dorr thickeners
- Continuous counter-current decantation
- Hydrocyclones
- Rotocel
- Kennedy extractor
- Bollman extractor
- Continuous horizontal extractor

Bollman Extractor
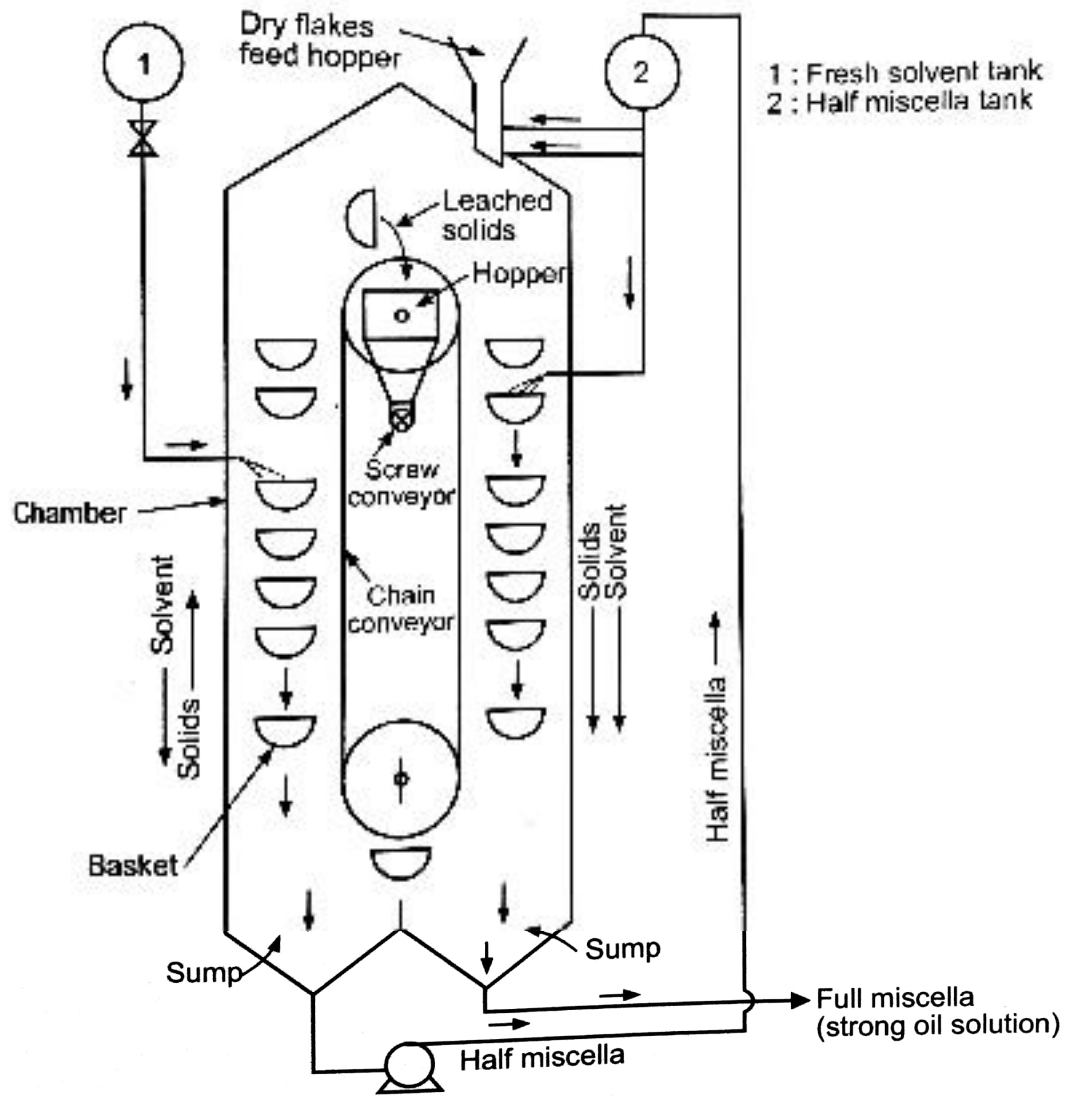
Bollman extractor

- Bollman Extractor is mainly used for the recovery of additional oil from the residues obtained after mechanical pressing of solids.

- The Bollman Extractor essentially consists of a vapour tight vertical chamber in which a series of perforated baskets are attached to a chain conveyor.

Bollman extractor

- The baskets are provided with perforations at the bottom.

- At the top right hand corner of the extractor solids are conveyed in to the perforated baskets. The baskets are loaded with flaky solids.

- These fully loaded baskets are then sprayed with Half Micelle as they travel downward through the right hand side.

- Half Miscella is the intermediate solvent containing some extracted oil and some small solid particles.

Bollman extractor

- As the solids and solvent flow co-currently down the right hand side of the machine, the solvent extracts more oil.

- Simultaneously the fine solids are filtered out of the solvent, so that the clean full miscella can be pumped from the outlet provided at the right hand bottom.

- Then as these partially extracted solids rise through the left hand side of the machine a stream of pure solvent is sprayed on them to obtain a dilute solution of the oil (half miscella) at the bottom of the chamber.

Bollman extractor

- This pure solvent percolates counter-currently through them and collects in the left hand sump which is then passed to the Half Miscella storage tank.

- The fully extracted solids are then dumped from the baskets at the top of the elevator to the hoppers from which they are removed by Screw Conveyors.

- Usually the conveyor speed is one revolution per hour.

Unit-IV:Adsorption

Adsorption

- The accumulation of molecular species at the surface rather than in the bulk of a solid or liquid is termed adsorption .

- The molecular species or substance, which concentrates or accumulates at the surface is termed **adsorbate** and the material on the surface of which the adsorption takes place is called **adsorbent.**
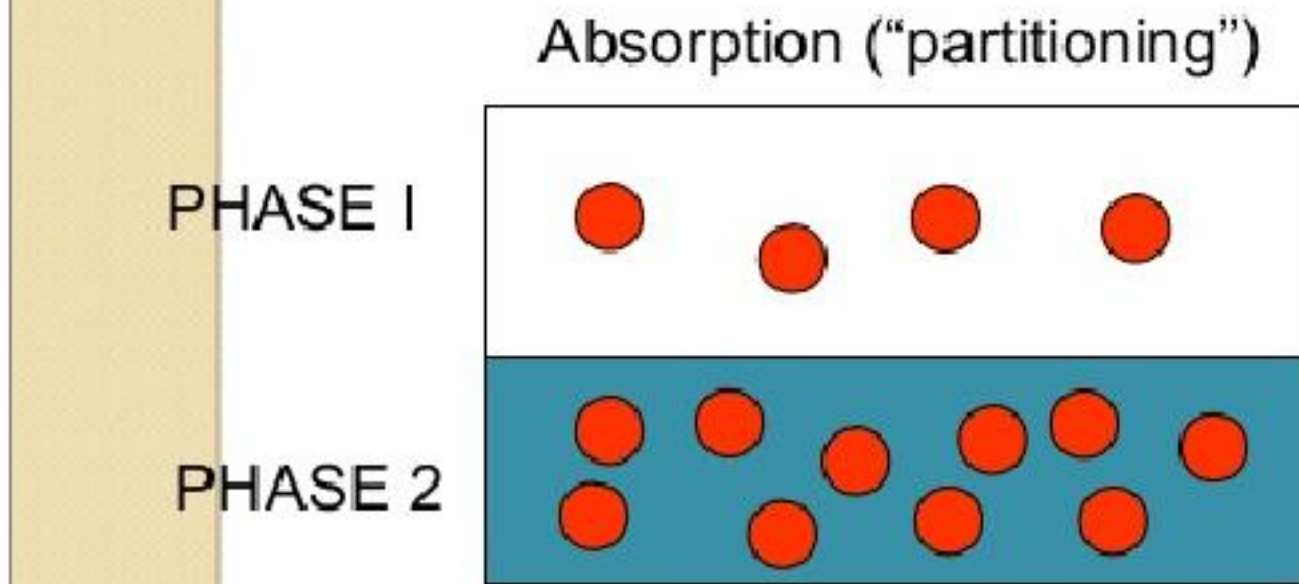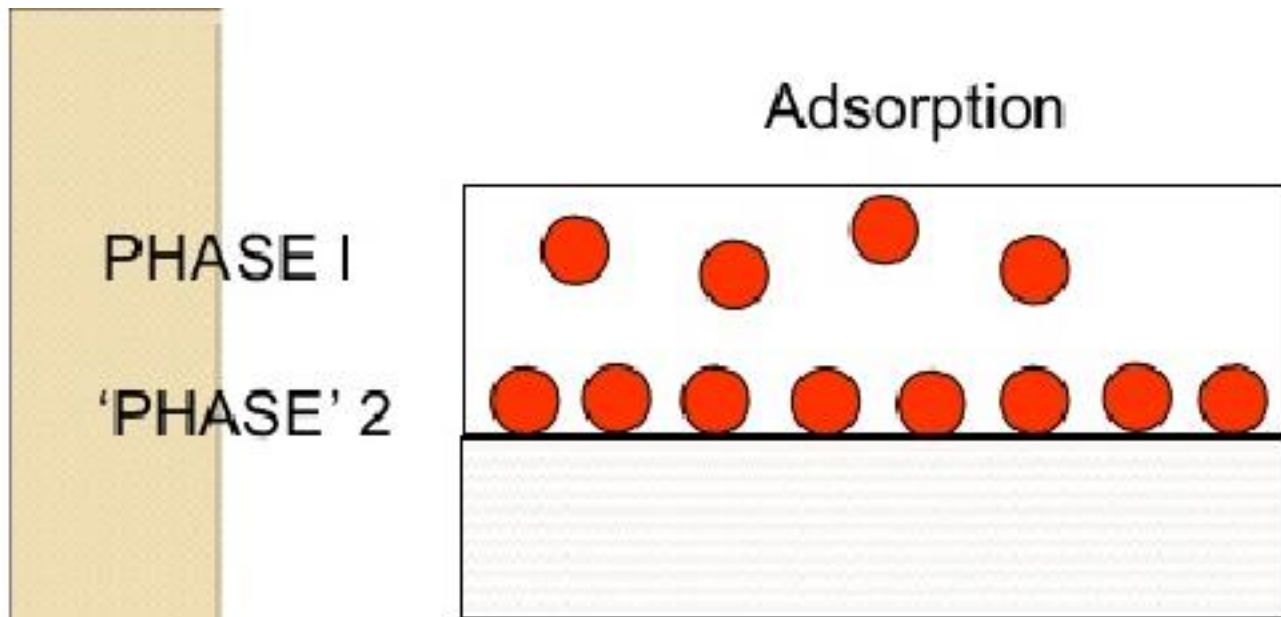
Action of adsorption

(i) If a gas like O_2, H_2, CO, Cl_2, NH_3 or SO_2 is taken in a closed vessel containing powdered charcoal, it is observed that the pressure of the gas in the enclosed vessel decreases. The gas molecules concentrate at the surface of the charcoal, i.e., gases are **adsorbed** at the surface.

(ii) In a solution of an organic dye, say methylene blue, when animal charcoal is added and the solution is well shaken, it is observed that the filtrate turns colourless. The molecules of the dye, thus, accumulate on the surface of charcoal, i.e., are adsorbed.

(iii) Aqueous solution of raw sugar, when passed over beds of animal charcoal, becomes colourless as the colouring substances are adsorbed by the charcoal.

(iv) The air becomes dry in the presence of silica gel because the water molecules get adsorbed on the surface of the gel.

The process of removing an adsorbed substance from a surface on which it is adsorbed is called desorption.

Adsorption Equilibrium

- Adsorption vs. Absorption
  - Adsorption is accumulation of molecules on a surface (a surface layer of molecules) in contact with an air or water phase
  - Absorption is dissolution of molecules within a phase, e.g., within an organic phase in contact with an air or water phase
- **adsorbate:** material being adsorbed
- **adsorbent:** material doing the adsorbing. (examples are activated carbon or ion exchange resin).

Adsorption

PHASE I

'PHASE' 2

Absorption ("partitioning")

PHASE I

PHASE 2

$$P_{gas} = K_H c_{aq}$$

Henry's Law

Adsorption versus Absorption

Physisorption or physical adsorption is a type of adsorption in which the adsorbate adheres to the surface only through Van der Waals (weak intermolecular) interactions, which are also responsible for the non-ideal behaviour of real gases.

Chemisorption in this kind of adsorption, the gas molecules or atoms are held to the solid by chemical bonds. For example hydrogen is chemisorbed on nickel.

Factors influencing adsorption

Adsorption of gases by solids

1. Adsorption and surface area

2. Nature of gas

3. Heats of adsorption

4. Reversible character

5. Effect of temperature

6. Effect of pressure

7. Thickness of adsorbed layer of gas

Factors influencing adsorption

Adsorption of gases by solids
1. Adsorption and surface area

Adsorption being a surface phenomenon, the extent of adsorption depends on the surface area. Increase in the surface area of the adsorbent, increase the total amount of the gas adsorbed.

2. Nature of gas

The amount of gas adsorbed by a solid depends on the nature of the gas. In general, more Easily liquefiable gas is more readily adsorbed.

3. Heats of adsorption

Heat of adsorption is defined as the energy liberated when 1gm mole of a gas is adsorbed on the solid surface. In physical adsorption, gas molecules concentrate on the solid surface. Thus it is similar to the condensation of a gas to liquid. Therefore, adsorption like condensation is an exothermic process.

4. Reversible character

Physical adsorption is reversible process. The gas adsorbed onto a solid can be removed under reverse conditions of temperature and pressure.

5. Effect of temperature

Physical adsorption occurs rapidly at low temperature and decreases with increasing temperature. Chemisorption, like most chemical changes, generally increases with temperature. Thus a rise of temperature can often cause physical adsorption to change to Chemisorption.

6. Effect of pressure

Pressure leads to increase of adsorption and decrease of pressure causes desorption.

7. Thickness of adsorbed layer of gas

The physically adsorbed gas forms only one molecular thick layer. However, above a certain pressure, multimolecular thick layer is formed.

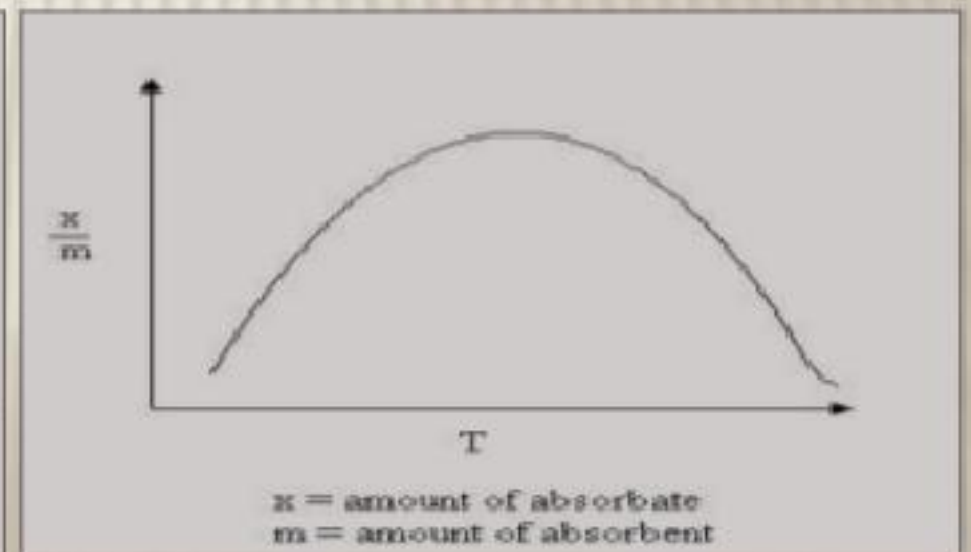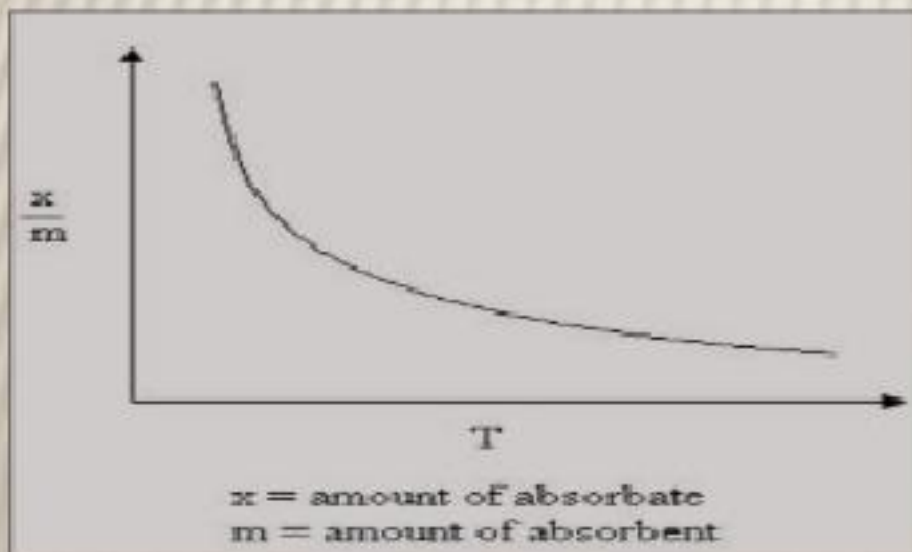| S.No	Physical adsorption	Chemical adsorption
1.	Caused by intermolecular forces	Caused by chemical bond formation
2.	Heat of adsorption is small	Heat of adsorption is large
3.	Reversible	Irreversible
4.	Forms multimolecular layer	Forms unimolecular layer
5.	Decreases with increasing temperature	Increases with increasing of temperature
6.	Depends on nature of gas	Much more specific than physical adsorption
7.	Increase of pressure increases adsorption, decrease of pressure causes of desorption	Change of pressure has no such effects

PHYSISORPTION / CHEMISORPTION

Physical Adsorption / Physisorption

a. Not very Specific
b. No electron transfer, although polarization of adsorbate may occur
c. Rapid, non-activated & reversible
d. No dissociation of adsorbed species
e. Monolayer or Multilayer
f. Only significant at relatively low temperatures
g. Enthalpies are in the region of -20 kJ/mol
h. As the temperature increases, process of Physisorption decreases

Chemical Adsorption/Chemisorption

a. Highly Specific
b. Electron transfer leading to bond formation between adsorbate & adsorbent
c. Activated, may be slow & irreversible
d. May involve dissociation
e. Monolayer only
f. Possible over a wide range of temperatures
g. Enthalpies are in the region of -200 kJ/mol
h. With the increases in temperature, Chemisorption first increases & then decreases

$\frac{x}{m}$ T

x = amount of absorbate
m = amount of absorbent

$\frac{x}{m}$ T

x = amount of absorbate
m = amount of absorbent

FACTORS AFFECTING ADSORPTION

TEMPERATURE

Adsorption is an exothermic process. Therefore in accordance with Le Chatelier's principle, the magnitude of adsorption should increases with decrease in temperature. It is in the case of physical adsorption. Chemical adsorption first increases with rise in the temperature and then starts decreasing ⭐

PRESSURE

With increase of pressure, adsorption increases up to certain extent till saturation level is achieved - no more adsorption takes place no matter how high the pressure applied.

SURFACE AREA

It's a surface phenomenon therefore adsorption capacity of adsorbent increases with increase in its surface area. Smaller the size of particles of solid adsorbents more is the extent of adsorption at its surface interface

ACTIVATION OF SOLID ADSORBENT

Activation of adsorbent surface done so as to provide more vacant sites on surface. This can be done by breaking solid crystal in small pieces, breaking lump of solid into powders or sub- dividing the adsorbent
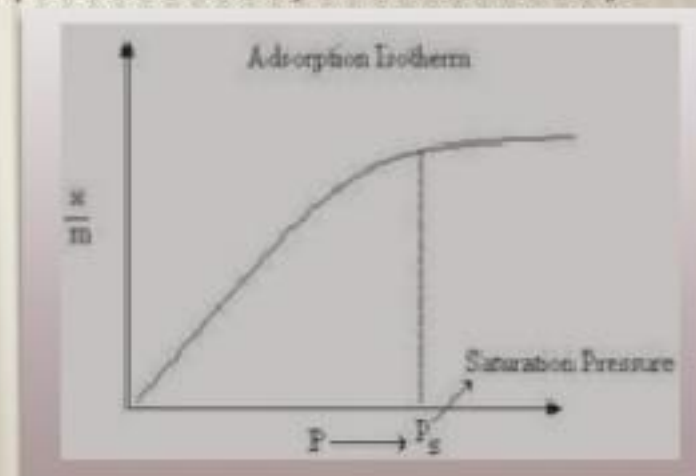
ADSORPTION ISOTHERMS

*Adsorption process is usually studied through graphs known as **Adsorption Isotherm**. The amount of adsorbate on the adsorbent as a function if its pressure (gas) or concentration (liquid) at constant T*

$$\textbf{ADSORBATE} + \textbf{ADSORBENT} \underset{\text{Desorption}}{\overset{\text{Adsorption}}{\rightleftharpoons}} \textbf{ADSORPTION}$$

➤ *According to **Le Chatlier's principle,** on application of excess pressure , the equilibrium will shift in the direction where number of molecules decreases.*

➤ *Since no. of molecules decreases in forward direction i.e. direction of **Adsorption** , with increase of pressure , forward direction equilibrium will be achieved*

➤ *In the given **Adsorption Isotherm** , after saturation pressure Ps adsorption does not increases*

➤ *Vacancies on the surface of the adsorbent are limited, at Ps a stage is reached when all the sites are occupied and further increase in pressure does not increases adsorption extent.*
Types of Adsorption Isotherms :

Adsorption Isotherm

$\dfrac{x}{m}$

Saturation Pressure

$P \longrightarrow P_s$

Graph between the amounts of adsorbate (x) adsorbed on the surface of adsorbent (m) and pressure at constant temperature

1. FREUNDLICH ISOTHERM   2. LANGMUIR ISOTHERM   3. TEMKIN ISOTHERM   4. BET ISOTHERM

FREUNDLICH ISOTHERM

➤ Empirical equation for representing the isothermal variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure is Freundlich Adsorption Isotherm

$$x/m = kP^{1/n} \quad \textbf{OR} \quad x/m = kC^{1/n}$$ .... **FREUNDLICH ISOTHERM**

➤ x/m = adsorption per gram of adsorbent which is obtained by dividing the amount of adsorbate (x) by the weight of the adsorbent (m).

➤ P is Pressure, k and n are constants whose values depend upon adsorbent and gas at particular temperature.
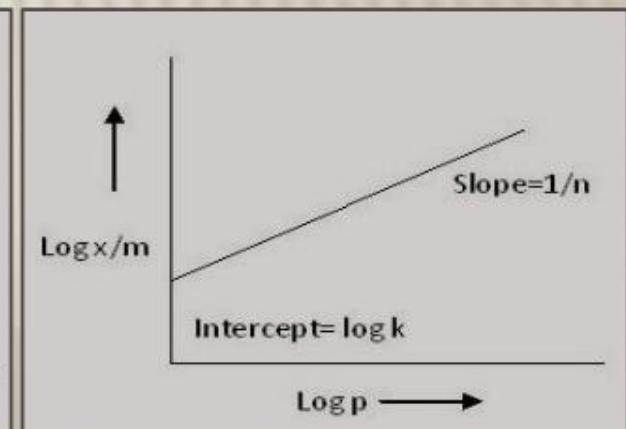
➤ Taking the logarithms of Freundlich Isotherm : $$Log\ x/m = log\ k + 1/n\ log\ P$$

➤ Freundlich Isotherm correctly established the relationship of adsorption with pressure at lower values,

Limitation : Failed to predict adsorption capacity at higher pressure
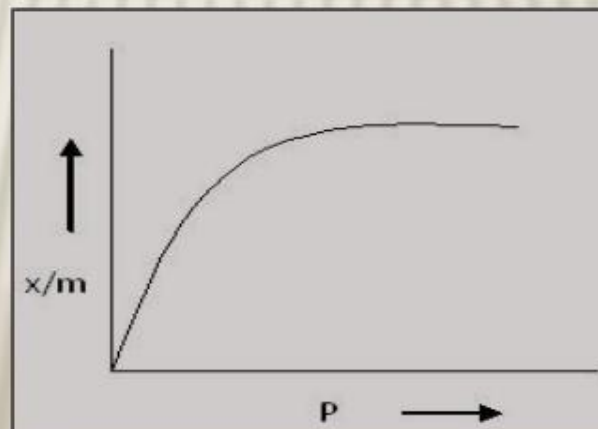
Freundlich Isotherm curve

Log x/m versus log P

Freundlich Isotherm:

- For the special case of heterogeneous surface energies (particularly good for mixed wastes) in which the energy term, "K_F", varies as a function of surface coverage we use the Freundlich model.

Langmuir Isotherm:

This model assumes monolayer coverage and constant binding energy between surface and adsorbate.

LANGMUIR ISOTHERM

In 1916, Langmuir proposed another Isotherm : **Langmuir Adsorption isotherm**

➢ Based on different assumptions one of which is that dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecule.

$$A(g) + M\ (surface) \rightleftharpoons AM\ (surface)$$

....
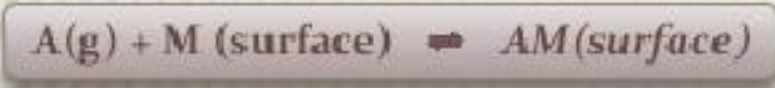
A(g) = unadsorbed gaseous molecules M(surface) = unoccupied adsorbent surface AM(surface) = Adsorbed gaseous molecules

➢ The extent of surface coverage is normally expressed as the fractional coverage, θ

θ = number of adsorption sites occupied / number of adsorption sites available

➢ The rate of change of surface coverage due to adsorption is proportional to the partial pressure p of gas & the number of vacant sites $N(1-\theta)$, where N is the total number of sites, k_a & k_d rate constants for adsorption & desorption

$$d\theta/dt = k_a\, pN(1-\theta)$$

....

Rate of Adsorption

➢ The rate of change of θ due to desorption is proportional to the number of adsorbed species, $N\theta$

$$d\theta/dt = -k_d\, N\theta$$

....

Rate of Desorption

➢ At equilibrium there is no net change (that is, the sum of these two rates is zero), and solving for θ gives the **Langmuir Isotherm**, where **K = (ka / kd)**

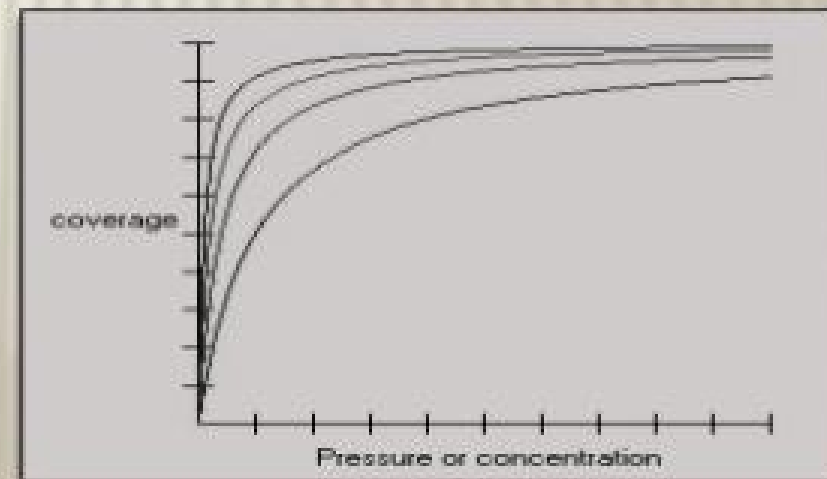$$\theta = Kp / (1 + Kp)$$ .... **LANGMUIR ISOTHERM**

➢ At lower pressure, Kp is so small that factor (1 + Kp) in denominator can almost be ignored & Langmuir equation reduces to :

$$\theta = Kp$$

➢ At higher pressure , Kp is so large that factor (1+ Kp) in denominator is nearly equal to Kp & Langmuir equation reduces to :

$$\theta = Kp / Kp = 1$$

Limitation : Valid at low Pressures only

coverage

Pressure or concentration

Langmuir isotherm for different values of K

Langmuir isotherm

In 1916, Irving Langmuir published an isotherm for gases adsorbed on solids, which retained his name. It is an empirical isotherm derived from a proposed kinetic mechanism. It is based on four hypotheses:

1. The surface of the adsorbent is uniform, that is, all the adsorption sites are equal.

2. Adsorbed molecules do not interact.

3. All adsorption occurs through the same mechanism.

4. At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.

Commonly Reported Adsorption Isotherms

Linear: $q = k_{\text{lin}} c$

Langmuir: $q = q_{\text{max}} \dfrac{K_L c}{1 + K_L c}$

Freundlich: $q = k_f c^n$
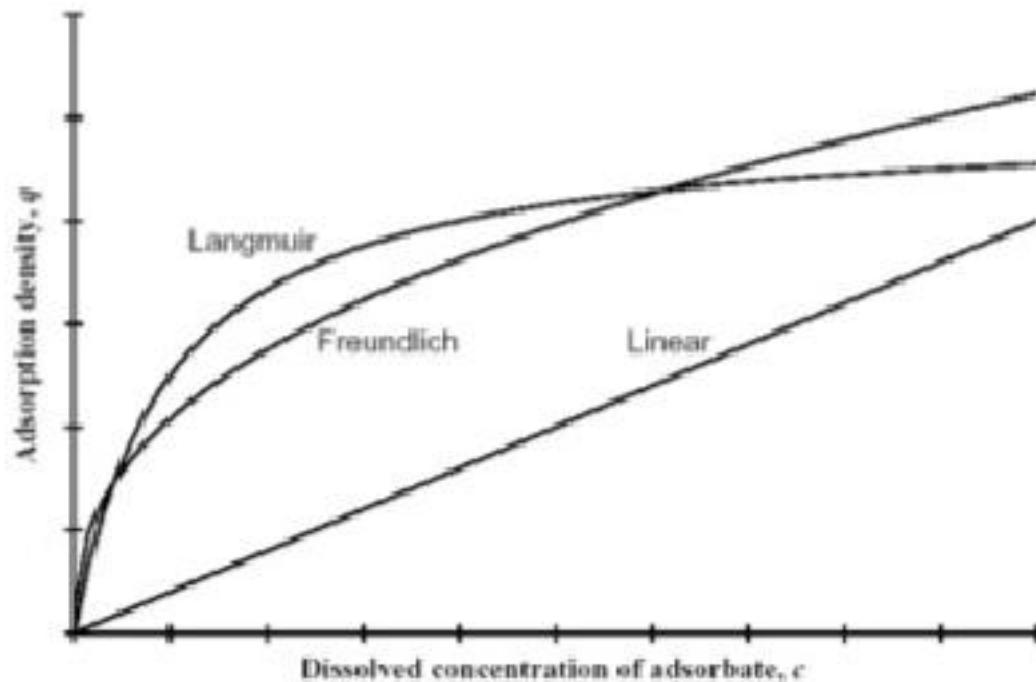
TYPES OF ADSORBENTS

Oxygen Containing Compounds

Typically Hydrophilic & Polar
Examples : Silica Gel & Zeolites

Carbon Based Compounds

Typically Hydrophobic & Non Polar
Examples : Activated Carbon &
Graphite

Polymer Based Compounds

Polar or Non polar functional
groups in a porous polymer matrix
Examples : Polymers & Resins

Another Classification is based on diameter of pore sizes of Adsorbents

Microporous Adsorbents

Pore Size Range
2 A° to 20 A°

Mesoporous Adsorbents

Pore Size Range
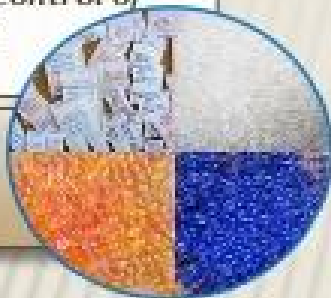20 A° to 500 A°

Macroporous Adsorbents
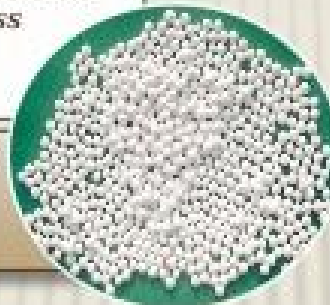
Pore Size Range
> 500 A°

COMMERCIAL ADSORBENTS

SILICA GEL

- Drying of refrigerants, organic solvents, transformer oils
- Desiccants in packing & double glazing
- Dew Point Control of natural Gas

ACTIVATED ALUMINA

- Drying of gases, organic solvents, transformer oils
- Removal of HCl from Hydrogen
- Removal of fluorine in Alkylation process

ACTIVATED CARBON

- Removal of odours from gases
- Recovery of solvent vapours
- Nitrogen from air
- Water purification
- Purification of He

POLYMERS & RESINS

- Water Purification
- Recovery & purification of steroids & amino acids
- Separation of fatty acids from water & toulene
- Recovery of proteins & enzymes

CLAY

- Treatment of edible oils
- Removal of organic pigments
- Refining of mineral oils
- Removal of poly chlorinated biphenyls (PCBs)

ZEOLITES

- Oxygen from air
- Drying of gases
- Drying of refrigerants & organic liquids
- Pollution control including removal of Hg
- Recovery of fructose from Corn Syrup

APPLICATIONS OF ADSORPTION

- ❏ Separation and purification of liquid and gas mixtures, bulk chemicals, isomers and air

- ❏ Drying gases and liquids before loading them in industrial systems

- ❏ Removal of impurities from liquid and gas media

- ❏ Recovery of chemicals from industrial and vent gases &

- ❏ **Water Purification**

Applications of adsorption

1. Production of high vacuum

If a partially evacuated vessel is connected to a container of activated charcoal cooled with liquid air, the charcoal adsorbs all the gas molecules in the vessel. This results in a very vacuum.

2. Gas mask

Gas masks are devices contain an adsorbent (activated charcoal) or a series of adsorbents; these adsorbents remove poisonous gases by adsorption and purify the air for breathing.

3. Heterogeneous catalysis

In a heterogeneous catalysis, the molecules of the reactant are adsorbed at the catalyst surface, where they form an "adsorption complex". This decomposes to form the product molecules which then take off from the surface.

4. Removal of coloring matter from solutions

Animal charcoal removes colours of solution by adsorbing coloured impurities thus in the manufacture of cane-sugar, the coloured solution is clarified by treating with animal charcoal or activated charcoal.

5. Chromatographic analysis

Mixtures of small quantities of organic substances can be separated with the help of chromatography which involves the principles of selective adsorption.

FIXED BED ADSORBERS

Raw Fluid In

Treated Fluid Out
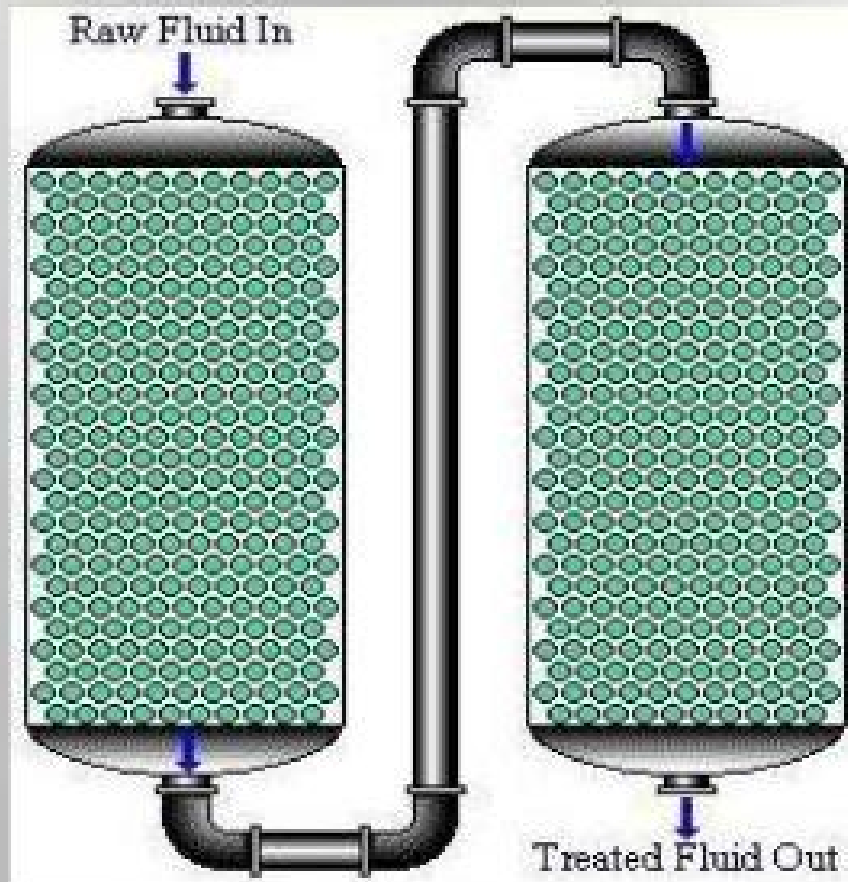
The fluid mixture to be treated is passed through a stationary bed of adsorbent.

As increasing amounts of fluid are passed through such a bed, the solid adsorbs increasing amounts of solute on its surface.
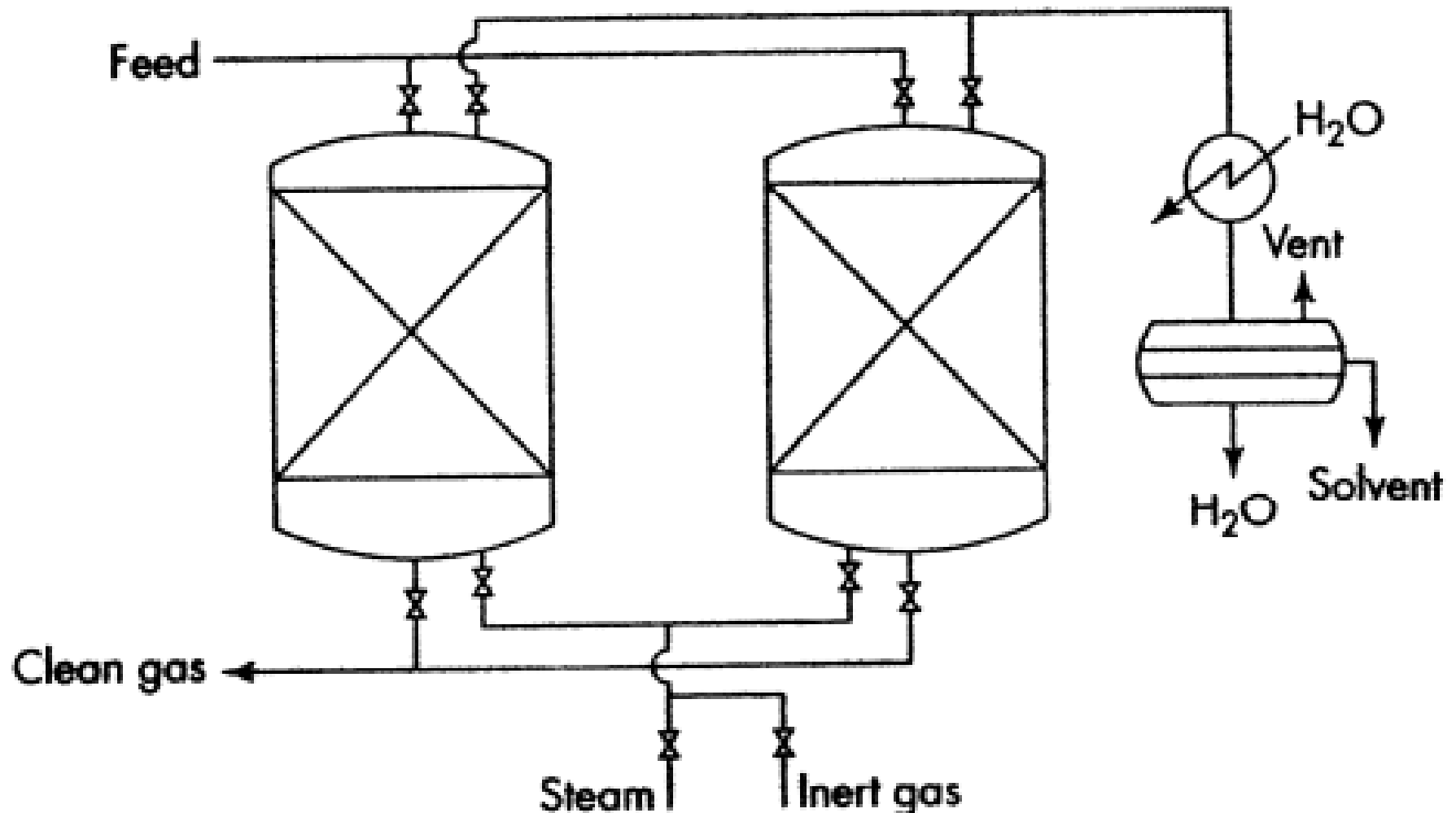
Fig. 1 Adsorption of solvent vapours in a fix bed system

Down flow is preferred, up flow might fluidise the particles (attrition and loss of fines)

In one column adsorption in the other desorption (regeneration of adsorbent) takes place.

- Regeneration is made with

- -steam (if the solvent is not miscible with water) or

- -hot inert gas

- Steam condenses in the bed, raises T of the solid and provides energy for desorption.

- The solvent is 1. condensed, 2. separated from the water, 3. sometimes dried before reuse.

- After regeneration the bed may be cooled and dried with inert gas.

- If some water vapour can be in the clean gas the evaporation of water remaining in the bed helps cool the bed during adsorption.