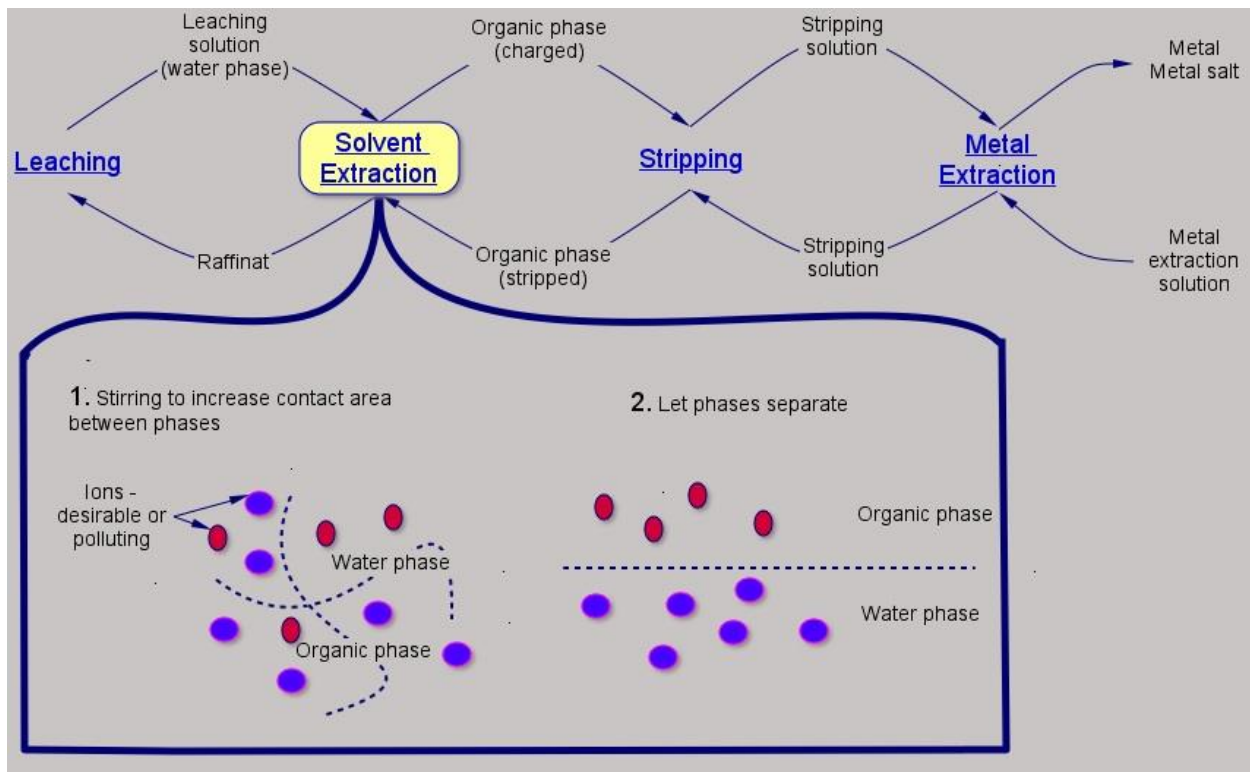


LECTURE # 10

Process



Essentially, solvent extraction consists of two circuits of non-miscible liquids put in contact, where a valuable metal in an aqueous solution is captured by an extractant in the organic phase.

Solvent extraction (SX) is a mass transfer operation and the technique used in metallurgical industry for selective extraction of metal ions from an aqueous solution. During the process, the desired metal ion is both purified and concentrated. An extractant capable of binding metal

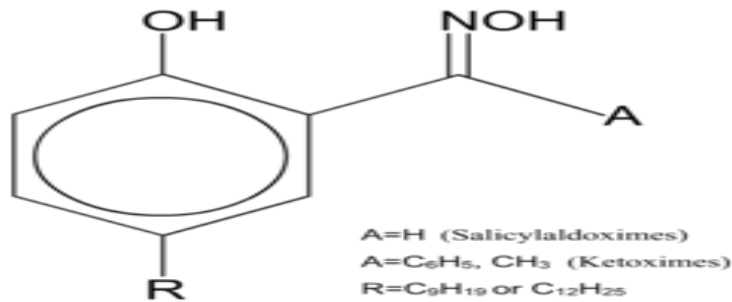
ions is dissolved in an organic kerosene type diluent. The extractant has an active hydrophilic group bound to a long chain hydrocarbon molecule in order to reduce solubility in the organic phase. The organic phase is then intensively mixed with the metal-bearing aqueous solution (feed) allowing the metal ions to bind to the extractant. The aqueous and organic phases are then allowed to separate and the wanted metal ion is now transferred to the organic phase. The extracted metal ion is then back-extracted (stripped) into a new aqueous phase in a pure and concentrated form. Ideally, only the desired metal transfers selectively from the aqueous phase to the organic phase.

Mechanisms

Depending on the properties of the extractant used and the chemistry of the metal-bearing solution, the extraction mechanism can be either cationic, anionic or solvating.

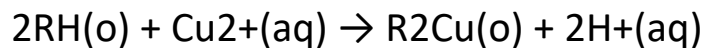
Cation extraction

Metal cations like Cu^{2+} , Zn^{2+} , Fe^{3+} , etc. are extracted. Typical extractants used are carboxylic acids, phosphoric acid compounds or hydroxyoximes (Fig). Different types of hydroxyoximes are used in commercial copper extraction from heap leaching of low grade copper ores.



HYDROXYOXIMES

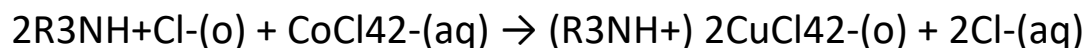
An example of Cu^{2+} extraction with a hydroxyoxime in sulphate environment is shown below:



The extraction is pH-dependent and copper is usually extracted at pH values of 1.5-2 and stripping is usually achieved with ~2M sulphuric acid. In practice, spent electrolyte from the electrowinning plant is used for stripping.

Anion extraction

Extraction of negative metal ion complexes like $CoCl_4^{2-}$, $CuCl_4^{2-}$, $FeCl_4^-$, etc.. Extractants are long chain amines with primary, secondary, tertiary or quaternary amine groups. An example of Co^{2+} extraction with a tertiary amine in chloride environment is shown below:

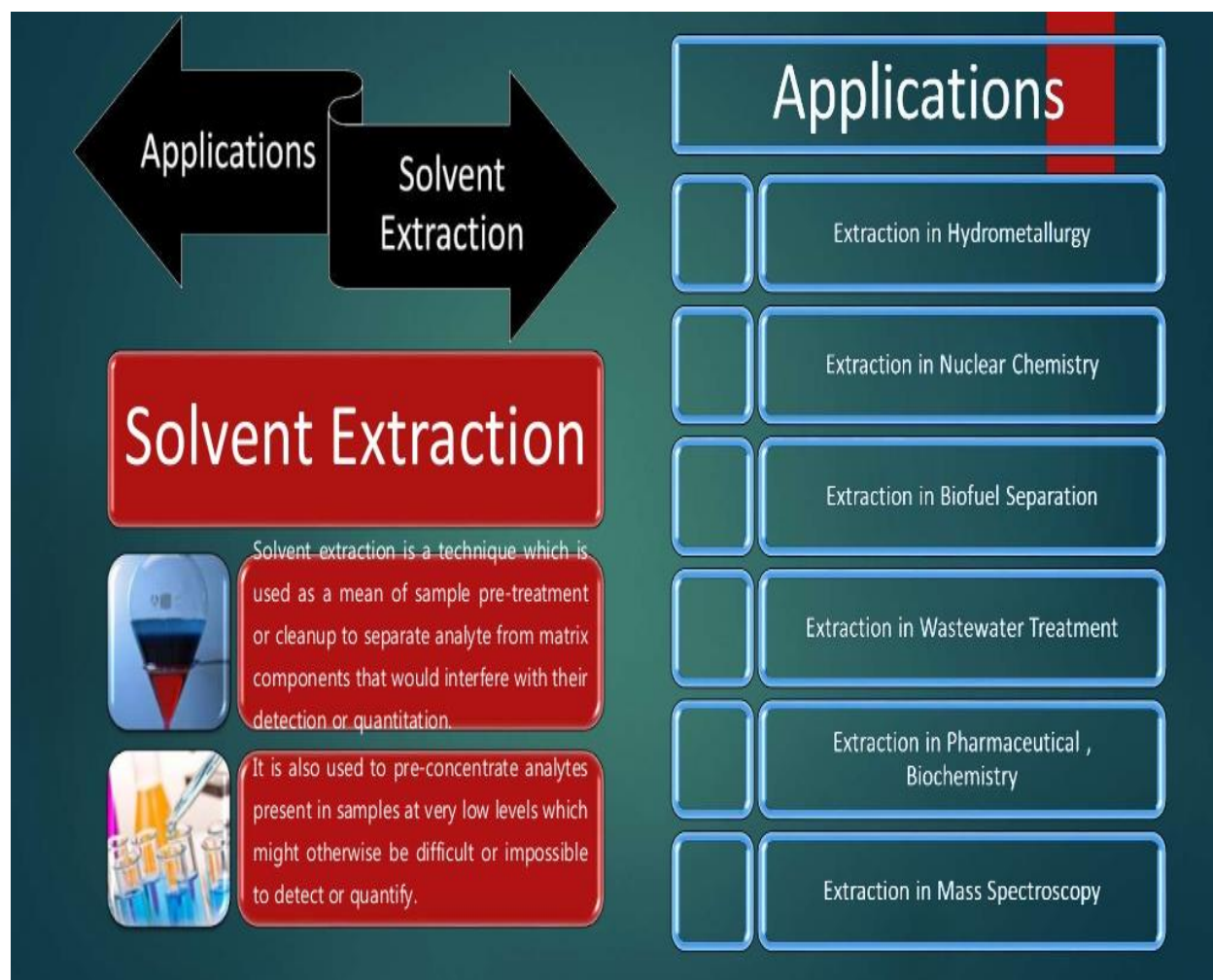


Extraction requires high chloride concentration so that the negatively charged cobalt chloride complex can form and stripping can be done with water.

Solvating extraction

Non-charged metal ion complexes are extracted. A typical extractant is tributylphosphate (TBP).

Application of Solvent Extraction



Extraction in Hydrometallurgy



Used electronic equipment became one of the fastest growing waste streams in the world. The most of the contemporary research activities on recovery of base and precious metals from waste PCBs are focused on hydrometallurgical techniques as more exact, predictable and easily controlled.



Hydrometallurgy is a technique which involves recycling of precious metals from used electronic equipment through leaching of substance with acids or bases.

Hydrometallurgical process

Leaching

- It involves the use of aqueous solutions to extract metals from metal bearing material which is brought into contact with a material containing a valuable metal.
- It involves five basic leaching reactors i.e In-situ, heap, vat, tank and autoclave

Concentration

- After leaching next is concentration of metal ions that are to be recovered.
- It involves precipitation, cementation, solvent extraction, ion exchange.

Recovery of metals

- The final step of hydrometallurgical process. Metals suitable for sale are often directly produced in the metal recovery step.
- Primary steps of metal recovery processes are electrolysis, gaseous reduction and precipitation.

Solvent Extraction application in nuclear industry

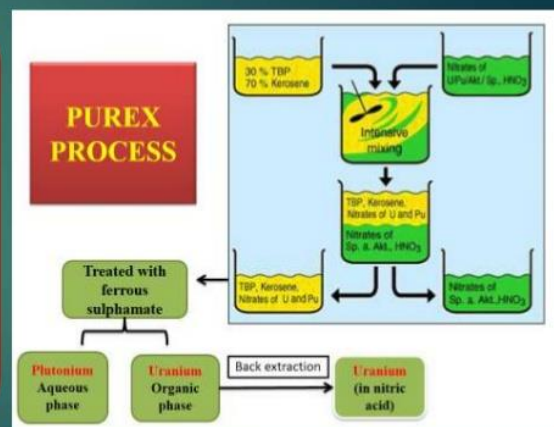
Composition of spent fuel

- Extraction of Uranium and Plutonium from spent nuclear fuel.
- Production of radionuclide



PUREX PROCESS (Plutonium and Uranium refining by extraction)

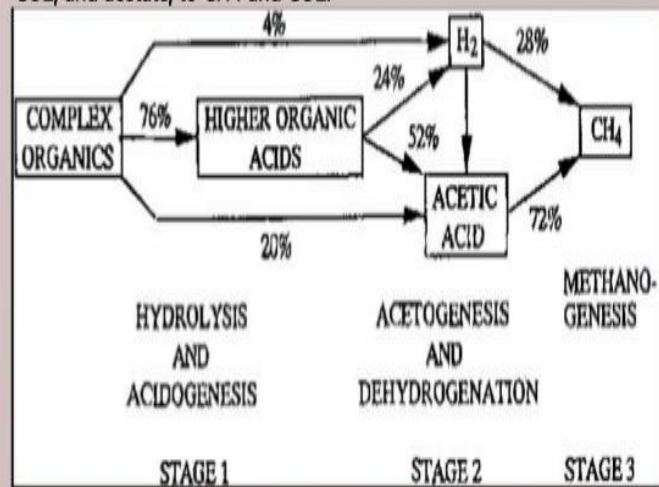
- Process for the reprocessing of spent nuclear fuel to separate uranium and plutonium from the fission products and from one another. Following the dissolution of the irradiated fuel in aqueous nitric acid, uranium and plutonium are transferred to an organic phase by intensive mixing with an organic solvent extraction - 30 percent tributyl phosphate (TBP) in kerosene is used as organic solvent - while the fission products remain in the aqueous nitric phase. Further process steps enable the subsequent separation of uranium and plutonium from one another.



Biogas extraction

Methane fermentation is a versatile biotechnology capable of converting almost all types of polymeric materials to methane and carbon dioxide under anaerobic conditions. This is achieved as a result of the consecutive biochemical breakdown of polymers to methane and carbon dioxide in an environment in which varieties of microorganisms which include fermentative microbes, hydrogen-producing, acetate-forming microbe, and methane-producing microbes (methanogens) grow and produce reduced end-products. Anaerobes play important roles in establishing a stable environment at various stages of methane fermentation.

- Methane fermentation offers an effective means of pollution reduction, superior to that achieved via conventional aerobic processes. Methane fermentation is the consequence of a series of metabolic interactions among various groups of microorganisms. The first group of microorganisms secretes enzymes which hydrolyze polymeric materials to monomers such as glucose and amino acids, which are subsequently converted to higher volatile fatty acids, H_2 and acetic acid. In the second stage, hydrogen-producing bacteria convert the higher volatile fatty acids e.g., propionic and butyric acids, produced, to H_2 , CO_2 , and acetic acid. Finally, the third group, methanogenic bacteria convert H_2 , CO_2 , and acetate, to CH_4 and CO_2 .



Extraction in biofuel

Biodiesel extraction methods

Biodiesel as one from important biofuel types is made from vegetable oils and animal fats. Biodiesel can be used as a fuel for vehicles in its pure form, but it is usually used as a diesel additive to reduce levels of particulates, carbon monoxide, and hydrocarbons from diesel powered vehicles. Biodiesel is produced from oils or fats using transesterification and is the most common biofuel.

• Transesterification:

- For the synthesis of biodiesel, the following materials were used: oil sample, methanol, and potassium hydroxide (KOH) as a catalyst. Methanol and potassium hydroxide were pre-mixed to prepare potassium methoxide, and then added to oil in the reactor with a mixing speed of 400 rpm for 2 h at 50 °C. The molar ratio of oil to methanol was 1:10. Finally, the mixture was left overnight to settle forming two layers, namely: biodiesel phase (upper layer) and the glycerin-rich phase (lower layer).



Solvent extraction in waste water treatment

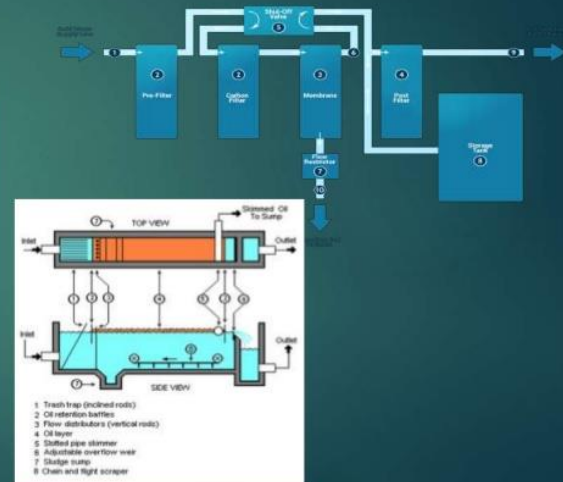
There are several contaminations in waste water playing important role. Many kinds of organic compounds such as pesticides, herbicides, phenols, PAHC, heterocyclic and aromatic compounds are included in the waste water.

- Industrial and agriculture production , and people living could be the source of organic waste water.
- Classic poisonous substances in organic waste water include the following;
 - Water organic matter
 - Formaldehyde
 - Phenols
 - Nitrobenzene
 - PCB's
 - PAH's etc.

Common form of chemical extraction using organic solvent as the extractant

Two major extraction techniques for wastewater treatment

- Solute solvent separation**
Reverse osmosis system is the best example of solute solvent extraction for treatment of waste water in various industries.
- Water solvent separation**
This type of separation is based on density gradient technique as the solvent forms separate layer above the water because of low density.
- Phenol removal, oily water desalination etc**



Solvent extraction in pharmaceutical and biochemical

Purification of pharmaceutical proteins

- Human insulin-like growth factor (IGF-1)
- Can be separated through solvent extraction.
- An aqueous two-phase extraction procedure was used which partitions soluble non-active (IGF-1) and biomass solids into separate liquid phases.

Partitioning of amino acids and oligopeptides

- Amino acids are constituents of proteins. Not only amino acids are partitioned by aqueous two phase system but also proteins can be separated.
- Production and partitioning of lactic acid can also done by aqueous two phase system

Purification of pharmaceuticals from plants

Ecdosyne and 20-hydroxyecdosyne, hormones both are steroids but soluble in water.

Their partitioning behavior was manipulated by adding ethanol, sodium chloride or sodium sulphate to the primary two-phase system.

The recovery of Ecdosyne increased when ethanol was added to the system.

Partitioning of porphyrin compound can also done by aqueous two-phase system.

Applications of extraction in the drug analysis



58

5. Studying of formation constant of complexes
 6. Studying of substance condition in a solution (a charge, polymerisation degree)
- Separation – controlled by pH which controls ionization and complex formation
 - Clean up before analysis
 - Preconcentration: Extract from a large aqueous volume into a much smaller organic volume.
 - *treatment of extracts, tinctures, antibiotics, preparations from a different biological material.*

Dr. Archana Naik, Saraswati Vidy Bhavans College of Pharmacy