HEAVY METALS AND THEIR SOURCES

• The most commonly encountered toxic heavy metals in wastewater:
  • Arsenic, Lead, Mercury, Cadmium
  • Less common: Chromium, Copper, Nickel, Zinc

• Sources
  • Industrial sources: e.g. Printed board manufacturing, metal finishing and plating, semiconductor manufacturing, textile dyes
  • Street runoffs
  • Landfills
PROBLEMS CAUSED BY HEAVY METALS

• Many heavy metals are essential trace elements for humans, animals and plants in small amounts

• In larger amounts cause acute and chronic toxicity.

• Linked to learning disabilities, cancers and even death

• Heavy metals have inhibitory effects on the biological treatment process at the wastewater treatment plants

• Limit the use of biosolids as fertilizer and may inhibit the digestion process in biogas plant
THE OCCURRENCE OF HEAVY METALS IN NATURE AND WASTEWATERS

- Many heavy metals occur also naturally.
- Contribution from human activities important for lead, cadmium and nickel.
- Measurements from the bottom sediments of the Golf of Finland suggest that highest pollution occurred during 1970-1980, a 40% decrease in recent sediments.
- The heavy metal concentrations in treatment plant sludges have decreased.
WAYS OF MINIMIZING THE CONCENTRATIONS OF HEAVY METALS

• Pretreatment of industrial effluents
  • More cost-effective and easier treatment
  • Recovery possible

• Agreements for industrial effluents with fixed limits for heavy metals

• Control samples from effluents

• Examples of used limits
  • Cd < 0,01 mg/l; Ni < 0,5 mg/l
  • Pb < 0,5 mg/l; Zn < 3,0 mg/l
REMOVAL OF HEAVY METALS AT THE MUNICIPAL WASTEWATER TREATMENT PLANT

- Activated sludge process does not remove most of the heavy metals efficiently
- Inhibition at high concentrations
- More load mainly from the use of chemicals
- Heavy metals do not disappear nor react – they are either in the water or in the sludge!
• Chemical precipitation
  • Hydroxide precipitation NaOH or Ca (OH)$_2$, pH 8 – 11
  • Addition of coagulants possible
  • + 99 % removal possible
  • Requires high concentration, produces sludge, some metal hydroxides are amphoteric, inhibition by complexing agents
  • Also sulfide precipitation (possible using sulfate-reducing bacteria), chelates

(Rast, 2013)
REMOVAL OF HEAVY METALS 2/3

• Ion exchange
  • High efficiency, fast process
  • Synthetic resins are most common
  • Research with natural zeolite
  • – cost-effective at high concentration, secondary pollution from regeneration

• Adsorption
  • Activated carbon – price increasing
  • Carbon nanotubes (CNT)
  • Low-cost or bioadsorbents (e.g. zeolite, clay; potato peels, eggshell, banana peels etc.)
  • Separation of biosorbents still a problem
REMOVAL OF HEAVY METALS 3/3

• Membrane filtration
  • Ultrafiltration, nanofiltration, reverse osmosis
  • Micellar enhanced (MEUF) = addition of surfactants to wastewater beyond the critical concentration, recovery and reuse of surfactant?
  • polymer enhanced (PEUF), research stage
  • NF&RO, high energy cost and membrane restoration

• Flotation
  • Ion flotation = imparting the ionic metals hydrophobic and removal by air bubbles

• Electrochemical methods
  • Electrocoagulation (Fe or Al electrodes)
  • Electroflotation (water electrolysis)
  • Electrodeposition (recovery)
REACHING VERY LOW LEVELS OF HEAVY METALS IN THE EFFLUENT

• EU priority substances with environmental quality standards:
  • Mercury < 5 µg/l; 0,05 µg/l
  • Lead ; 7,2 µg/l
  • Cadmium < 10 µg/l ; 0,08 – 0,25 µg/l
  • Nickel ; 20 µg/l
• Concentrations in Finnish treated wastewater typically
  • Cd < 0,5 µg/l; Hg < 0,2 µg/l
  • Pb < 3 µg/l ; Ni < 10 µg/l
ANALYSING HEAVY METALS IN WASTE WATER

- Waste water samples are usually digested using microwave digestion in aqua regia or strong nitric acid.
- Analyses of the elements are performed using ICP-MS technique.
- Method is based on the SFS-EN ISO 17294-2 standard.
ICP-MS (INDUCTIVELY COUPLED PLASMA MASS SPECTROMETER)

• The digest solution is nebulized and sample aerosol is transported to argon plasma

• High temperature plasma produce the ions, which are introduced into the mass spectrometer

• The mass spectrometer sorts the ions according to their mass-to-charge ration and the ions are quantified with an electron multiplier detector
THANK YOU! KIITOS!