Methods of pollution control and waste management

Lecture 1

Introduction and water treatment processes

The main issues to be covered

- **Environmental chemistry**
  - Environmental composition
  - Chemical processes
  - Anthropogenic effects
  - Global perspective
- **Hydrosphere**
  - Global distribution of water
  - Water pollution and water treatment chemistry
  - Wastewater treatment methods
- **Methods of pollution control**

The main issues to be covered

- Energy Sources and Environmental Effects
- Stratosperic chemistry
- Troposperic chemistry
- Methods of sulfur and nitrogen oxides control
- VOCs treatment methods
- Solid waste management – treatment methods and legislation
  - ➢ Plastics
  - ➢ Municipal waste
  - ➢ Industrial waste
  - ➢ Radioactive waste

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Lecture materials:
http://www.chem.uw.edu.pl/people/EMegiel/lecture

Login: Lecture
Passwd: Environment

Office hours: Tuesday
15.00÷16.00, room 134

Recommended literature
G. W. van Loon, S. J. Duffy “Environmental chemistry” Oxford Press 2011.
G. W. van Loon, S. J. Duffy “Environmental Chemistry: A Global Perspective” Oxford Univesity Press, 2005.

20th of November – written mid-term test
27th of November (11.45)- first lab
22th of January – written exam

Environmental chemistry

The study of the sources, reactions, transport, effects, and fates of chemical species in the water, soil and air environment, as well as the influence of human activity upon these processes.

Pollutant – substance present in greater than natural concentration as a result of human activity.

Waste – according to European Directive 75/442/EC substance or object the holder discards, intends to discard or is required to discard.

Environmental chemistry

- Hydrosphere
- Lithosphere
- Atmosphere
- Biosphere
- Pedosphere (soil chemistry)

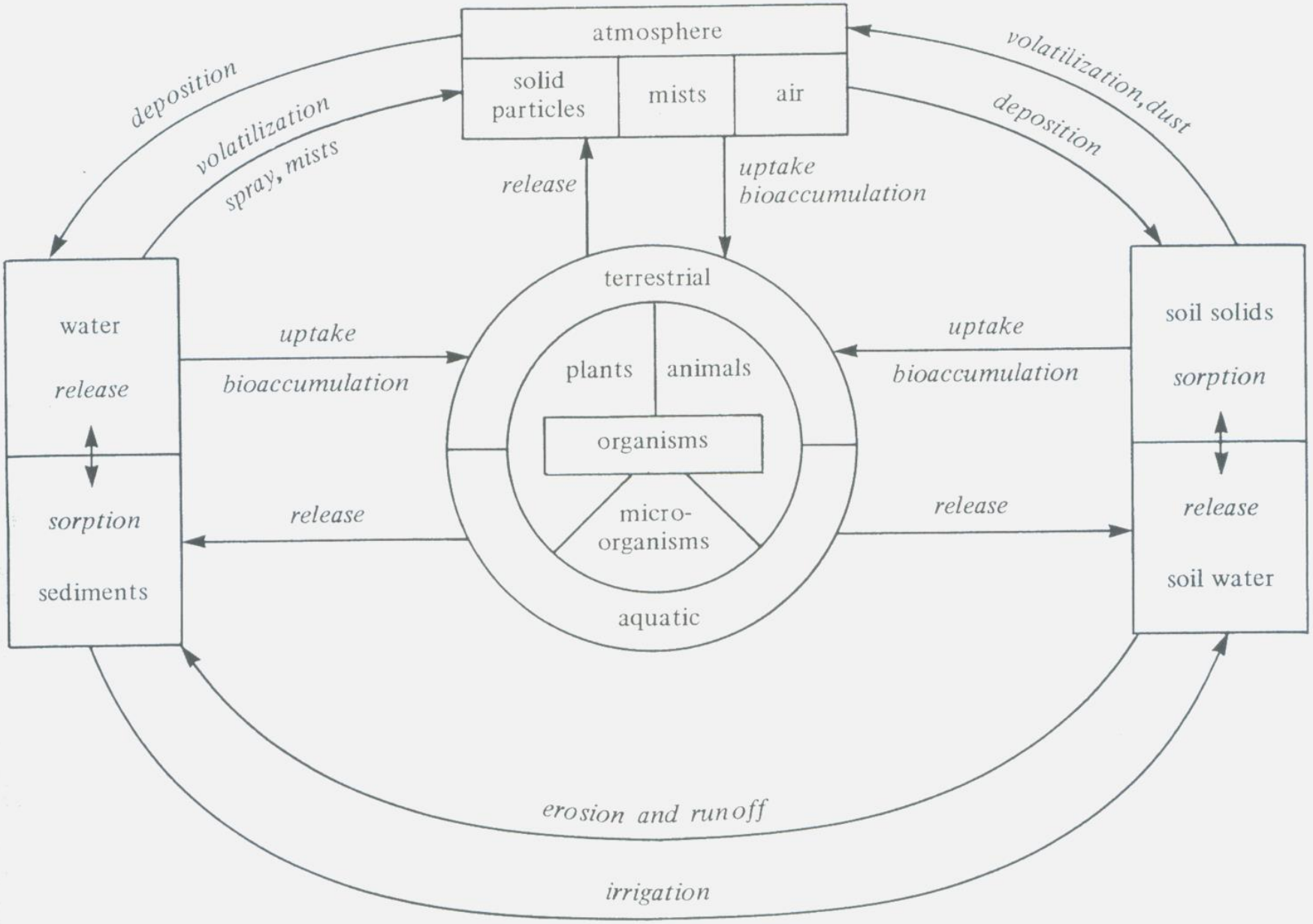
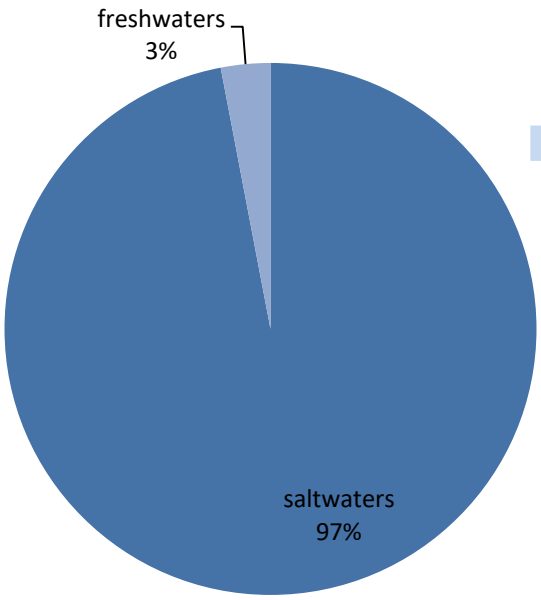


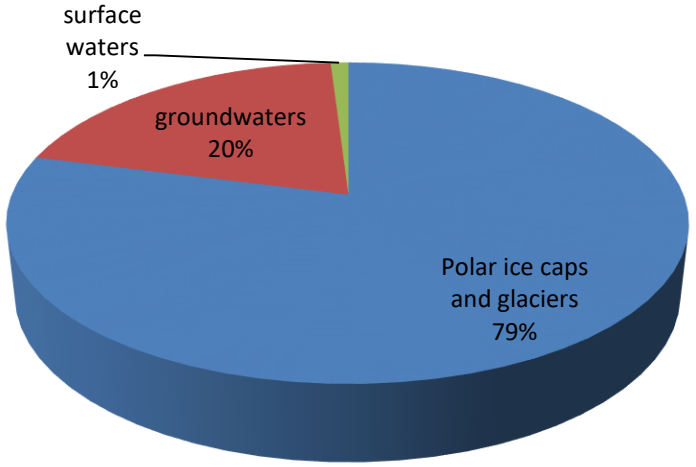
FIGURE 7.1 Pollutant cycles in the environment.

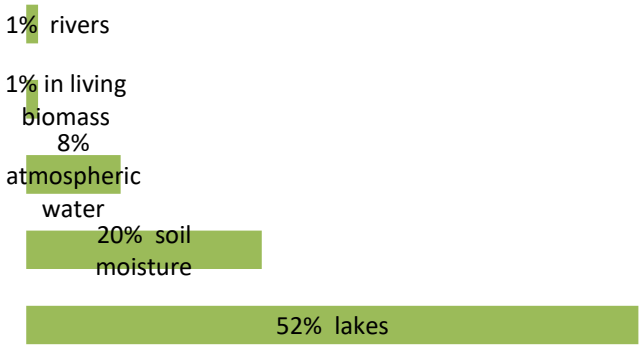
S. E. Manahan „Environmental Chemistry" Brooks/Cole Publishing Company , 1984

Hydrosphere

70 % of the earth's surface is covered by water almost three times as much as the continents
The availability of the water for human consumption is strongly limited.







G. W. vanLoon&S. J. Duffy „Environmental Chemistry a global perspective, Oxford University Press, 2011

Important properties of Water

Property	Effects and significance
Excellent solvent	Transport of nutrients and waste products, making biological processes possible in an aqueous medium
Highest dielectric constant of any pure liquid	High solubility of ionic substances and their ionization in solution
Higher heat capacity than any other liquids except ammonia	Stabilization of temperatures of organisms and geographical regions
Transparent to visible and longer wave-length fraction of ultraviolet light	Colorless, allowing light required for photosynthesis to reach considarable depths in bodies of water
Maximum density as a liquid at 4^0C	Ice floats, vertical circulation restricted in stratified bodies of water
Higher surface tension than any other liquid	Controlling factor in physiology, governs drop and surface phenomena

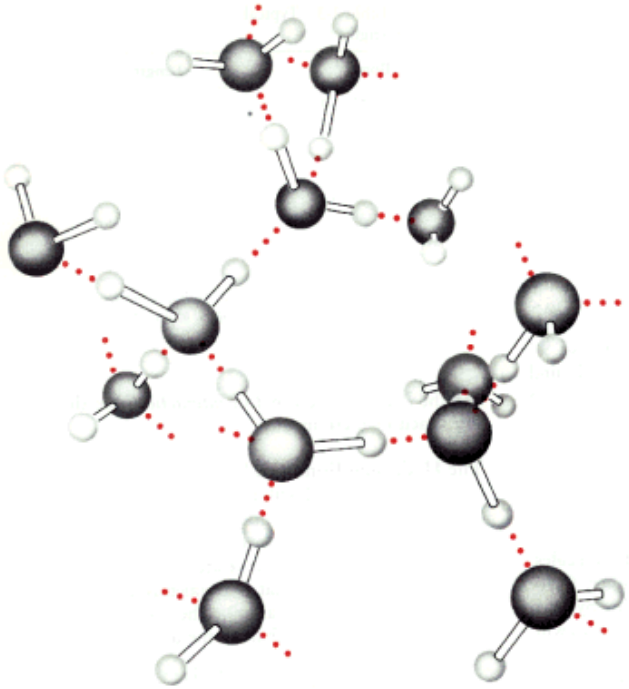
G. W. vanLoon&S. J. Duffy „Environmental Chemistry a global perspective, Oxford University Press, 2011

Important properties of water

- Hydrogen bondings in water

$\Delta H_{O....H}$=10-40 kJ/mol

The structure of ice takes the form of hexagonal rings and causes that density of ice is lower than liquid water.



When ice melts only 12% of hydrogen bonds are broken. Thus a relative large amount of heat is required to change the temperature of mass of water.

Water Pollution

- Pure H_2O doesn't exist in hydrosphere
- What is pollutant in water?

Substance or action which has a negative influence on the environmental, people health, their state of mind and mental state.

Classes of Water Pollution

Class of pollutant	Significance
Trace elements	Toxicity
Metal-organic combinations	Metal ion transport changed
Inorganic pollutants	Toxicity
Asbestos	Human health (pulmonary asbestosis)
Algal nutrients	Eutrophication (depletion of oxygen in a body of water which kills aquatic animals)
Radionuclides	Toxicity
Acidity, alkalinity, salinity (if in the excess)	Water quality, adverse influence on aquatic life
Sewage	Water quality, oxygen levels
Pesticides	Toxicity
Petroleum waste	Adverse effect on wildlife, esthetics
Detergents	Eutrophication, wildlife, esthetics
Pathogens	Health effects
Taste, odor, and color	Esthetics

G. W. vanLoon&S. J. Duffy „Environmental Chemistry a global perspective, Oxford University Press, 2011

Examples of trace elements

Element	Sources	Effects and significance
Arsenic	Mininig by product, pesticides, chemical waste	Toxic, possibly carcinogenic
Cadmium	Industrial discharge, mining waste	Replace zinc biochemically, causes high blood pressure, destroys red blood cells
Lead	Industry, mining, plumbing	Toxicity (anemia,kidney disease, nervous system)
Mercury	Industrial waste, pesticides	Acute and chronic toxicity
Selenium	Natural geological sources, accompanied sulfur, coal deposits	Essential at low levels, toxic at higher levels, causes alkali desease

G. W. vanLoon&S. J. Duffy „Environmental Chemistry a global perspective, Oxford University Press, 2011

Guidelines for quality of water

Drinking water quality standards determined by WHO (World Health Organisation)

Substance	Concentration [μg/dm^3] ppb
Inorganic substance	
As	10
B	300
Cd	3
Cr	50
Cu	2000
Hg	1
NO_3^-, NO_2^-	50, 3
Pb	10

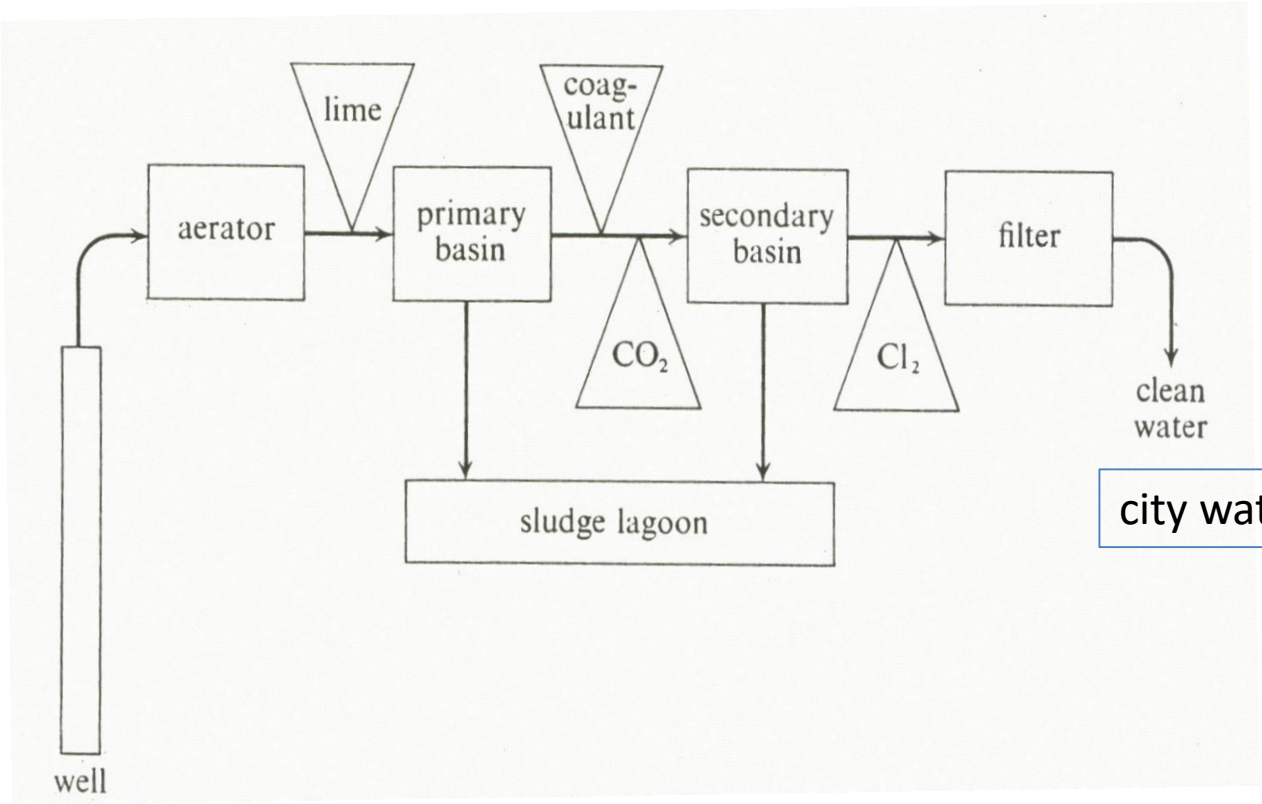
Selected substances from Guidelines for drinking water quality WHO Geneva 1993

Guidelines for quality of water

Substance	Concentration [μg/dm^3] ppb
Organic compounds	
Benzene	10
Benzopyrene	0.7
TCE (trichloroethylene)	70
DDT (pesticide)	2
Atrazine (pesticide)	2
Chloroform (solvent)	200

Selected substances from Guidelines for drinking water quality WHO Geneva 1993

Water treatment plant



city water mains

1. Removes volatile solutes: H_2S,CO_2, CH_4, oxidation soluble Fe(II) to unsoluble Fe(III) 2. raises pH and formation of precipitates containing the hardness ions Mg^{2+}, Ca^{2+} , 3. settles the colloidal particles 3. lower pH 4. disinfection

*S. E. Manahan „Environmental Chemistry" Brooks/Cole Publishing Company , 1984

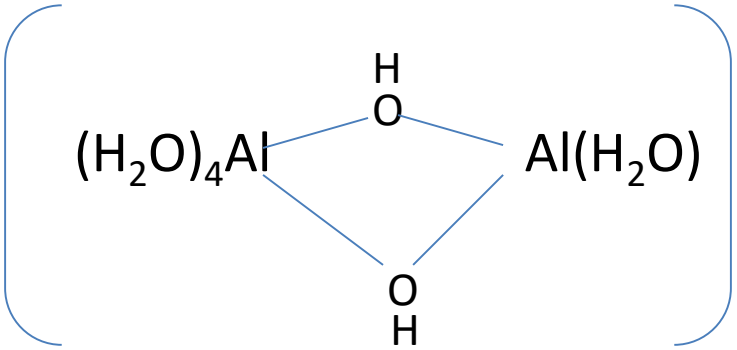
Removal of solids

- Settling and filtration (suspended relatively large particles)
- Addition of coagulants (coagulation-flocculation destabilization of colloids):

$Al_2(SO_4)_3 \cdot 18\ H_2O$, $FeSO_4 \cdot 7\ H_2O$, starch, celluloze, synthetic polymers

$$Al(H_2O)_6^{3+} + 3\ HCO_3^- \longrightarrow Al(OH)_3 + 3\ CO_2 + 6\ H_2O$$

$$Al(OH)_3 + OH^- \longrightarrow Al(OH)_4^-$$



positively charged ion interacts with colloidal particles bringing about coagulation

Hydrolyzed species of Al (III) and Fe(III) can cause coagulation by adsorption

Coagulation and flocculation

No Turbidity Colloid

- Colloidal impurities in surface water cause the water to appear turbid or may impart color
- It is diffucult to seperate colloids from water because:

→ Colloids do not settle by gravity

→ They are so small particles that pass through the pores of most common filtration media.

Coagulation and flocculation

- For the removal of colloids:

(The individual colloids must aggregate and grow in size)

- Coagulation: is the addition and rapid mixing of coagulant

→for destabilization of particles

→for initial aggregation of the destabilized particles

- Flocculation: is the slow stirring or gentle agitation

→to aggregate destabilized particles

→to form rapid settling floc

Removal of water hardness/softening

- For properly detergents function
- For limited of creation of mineral deposit which coats the surface of hot water systems, reducing heating efficiency and stopping water flow

$$Ca^{2+} + 2HCO_3^- \longrightarrow CaCO_{3(s)} + CO_2 + H_2O$$

$$Mg^{2+} + 2HCO_3^- \longrightarrow MgCO_{3(s)} + CO_2 + H_2O$$

Degree of water hardness

Germany (^{0}n) contents of calcium and magnesium salts equivalent of 10 mg CaO in 1 dm^3 water,

French (^{0}f) contents of calcium and magnesium salts equivalent of 10 mg $CaCO_3$ in 1 dm^3 water,

English (^{0} Clark's degree) contents of calcium and magnesium salts equivalent of 14,3 mg $CaCO_3$ in 1 dm^3 water

Removal of water hardness/softening

- Lime-soda process on a large scale

$Ca^{2+} + 2HCO_3^- + Ca(OH)_2 \longrightarrow 2CaCO_{3(s)} + 2\,H_2O$

$Ca^{2+} + 2\,Cl^- + 2\,Na^+ + CO_3^{2-} \longrightarrow CaCO_{3(s)} + 2\,Na^+ + 2\,Cl^-$

The precitipation of magnesium as hydroxide in higher pH

$CO_3^{2-} + H_2O \longrightarrow HCO_3^- + OH^-$

$Mg^{2+} + 2OH^- \longrightarrow Mg(OH)_2$

<u>Defects this method</u>:

Relatively high solubility product constant K_{so} for $CaCO_3$ and $Mg(OH)_2$ (significant amount of these compounds remain in solution)

Possible clouding in water

High pH of water after these processes (ca. 11) thus water have to be recarbonated by bubbling CO_2

Removal of water hardness/softening

Recarbonation after lime-soda process

$OH^- + CO_2 \longrightarrow HCO_3^-$

$CaCO_3 + CO_2 + H_2O \longrightarrow Ca^{2+} + HCO_3^-$

$Mg(OH)_2 + 2\ CO_2 \longrightarrow Mg^{2+} + 2\ HCO_3^-$ pH=7.5-8.5

Addition of phosphate (Na_3PO_4)

$5Ca^{2+} + 3\ PO_4^{3-} + OH^- \longrightarrow Ca_5OH(PO_4)_3$ hydroxyapatite pH > 10.5

$3Ca^{2+} + 2\ PO_4^{3-} \longrightarrow Ca_3(PO_4)_2$ orthophosphate pH < 10

Orthophosphates have solubility product constants smaller than carbonate

Removal of water hardness/softening

- **Ion exchange processes**

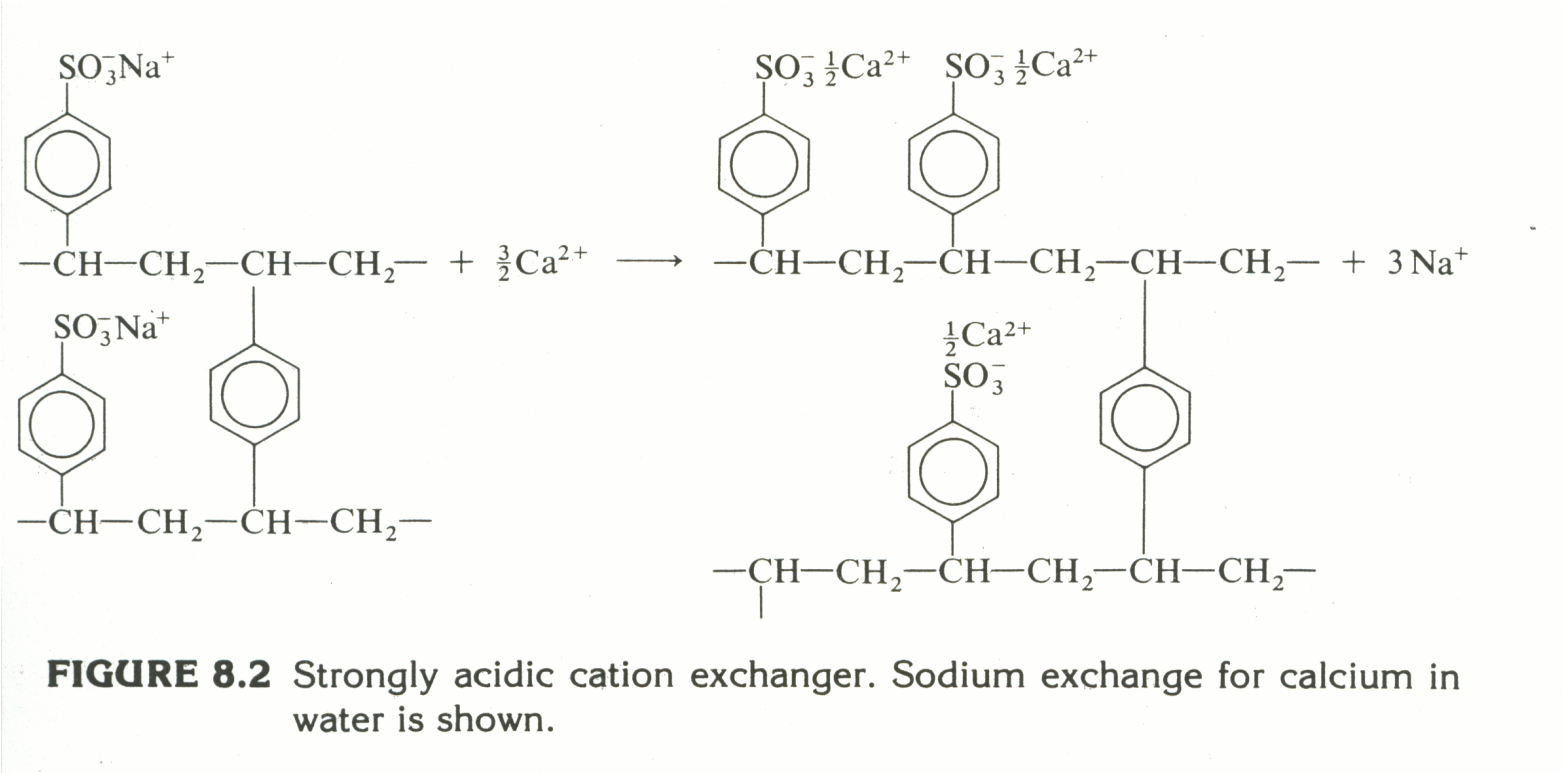


FIGURE 8.2 Strongly acidic cation exchanger. Sodium exchange for calcium in water is shown.

*S. E. Manahan „Environmental Chemistry" Brooks/Cole Publishing Company , 1984

Removal of water hardness//softening

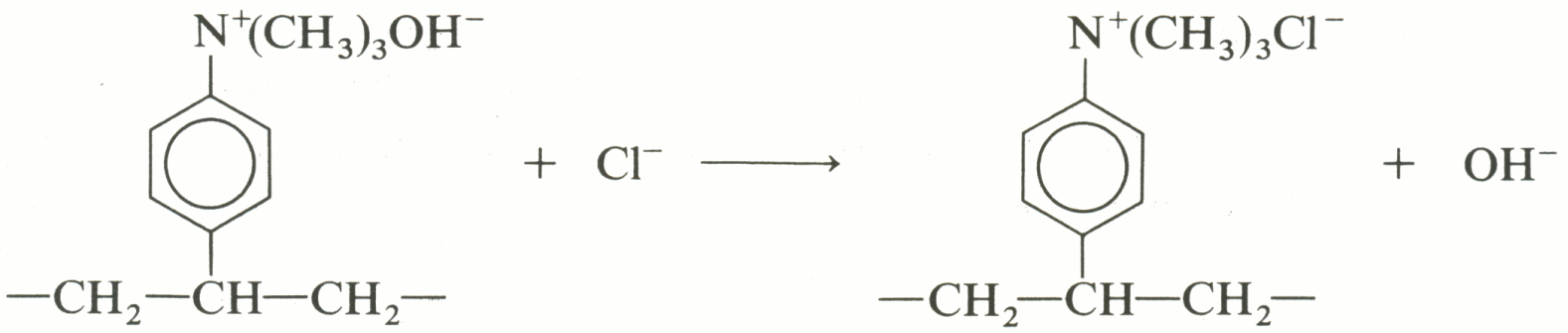


FIGURE 8.3 Strongly basic anion exchanger. Chloride exchange for hydroxide ion is shown.

It is possible to yield deionised water if water will be first passed over cation exchanger and next over anion exchanger.

Materials which have ion-exchanging properties: natural and synthetic zeolites microporous aluminosilicate), cross-linked polymers with active acidic or basic group.

*S. E. Manahan „Environmental Chemistry" Brooks/Cole Publishing Company , 1984

Removal of organics from drinking water

1 g AC has a surface area in excess of 500 m^2

Adsorption on activated carbon:

- granulated activated carbon 0.1 -1 mm in diameter
- Powdered activated carbon 50-100 μm (higher degree of microporosity)
- **Phenol value** – amount of carbon in miligrams required to reduce by 90% the phenol in 1 l of a solution containing 100 μg/l of phenol, (commercial 15-30)
- Regeneration of the carbon – heating to 950^0C in a steam air atmosphere

The mechanism by which activated carbon holds organic compounds is not exactly described, one reason for this process is large surface area of activated carbon.

DISINFECTION OF WATER

I. Chlorine addition (as $Cl_{2(aq)}$)

$$Cl_2 + H_2O \rightleftharpoons H^+ + Cl^- + HOCl \quad K_h = 4.5 * 10^{-4}$$

$$HOCl \rightleftharpoons H^+ + ClO^- \quad K_a = 2.7 * 10^{-8}$$

Hypochlorous acid — hypochlorite ion

HOCl oxidizes enzymes in bacteria cells.

K_a increasing with increasing pH values of solution, usually disinfection performed for pH ca 7

pH	% HOCl	Dose of chlorine g Cl_2/m^3
4	100	1.000
7	75.2	1.330
9	2.9	34.00

A. L. Kowal, M Świderska-Bróż, Oczyszczanie wody, PWN 2009

DISINFECTION OF WATER

II. Calcium hypochlorite $Ca(ClO)_2$ addition (solid)

- **DBPs (disinfection by-products) mainly** trihalomethanes. Chlorine produces a number of by-products in the presence of organic matter in water. $CHCl_3$ is the most important.

III. **Chlorine dioxide ClO_2** gas, free radical, powerful oxidizing agent, oxidizing organic compounds, produce a much smaller DBPs compared chlorine and hypochlorite

Chronic chloroform exposure can damage the liver (where chloroform is metabolized to phosgene) and the kidneys.

$$ClO_2 + 4H_3O^+ + 5e \longrightarrow Cl^- + 6H_2O$$

DISINFECTION OF WATER

Chloroamines - combined available chlorine

$NH_4^+ + HOCl \longrightarrow NH_2Cl + H_2O + H^+$

$NH_2Cl + HOCl \longrightarrow NHCl_2 + H_2O$

$NHCl_2 + HOCl \longrightarrow NCl_3 + H_2O$

- NH_2Cl, $NHCl_2$, NCl_3 weaker disinfectant than chlorine (water distribution system)
- Kind of product depend on molar ratio Cl_2:NH_4^+ and pH
- Chlorination with 8:1 weight ratio Cl: NH_3 denitrification

$2NH_2Cl + HOCl \longrightarrow N_2 + 3\,H^+ + 3\,Cl^- + H_2O$