

# ***Advance Groundwater Treatment Iron, Manganese, Fluoride and Boron Removal***

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# ***Groundwater as a Source for Drinking Water Production***

- **97% of the planet's freshwater stored in aquifers**
- **groundwater in general of constant & good quality**
- **commonly available close to demand points**
- **relatively low capital & operational costs**

# ***Groundwater Use for Drinking Water Production***

**The major source in many countries**

<b>Region</b>	<b>Share of GW (%) (%)</b>	<b>people served (million)</b>
<b>Asia / Pacific</b>	<b>32</b>	<b>1000-2000</b>
<b>Europe</b>	<b>75</b>	<b>200-500</b>
<b>Latin America</b>	<b>29</b>	<b>150</b>
<b>US</b>	<b>51</b>	<b>135</b>
<b>Australia</b>	<b>15</b>	<b>3</b>
<b>World</b>		<b>1.5-2.0 Billion</b>

# ***Groundwater Use for Drinking Water Production by Country***

## **Europe**

**Denmark 100%, Germany 72%, The Netherlands 68%  
The United Kingdom 27%**

## **Asia**

**India (rural) 80%, Philippines 60%, Thailand 50%,  
Nepal 60%, Bangladesh 90%**

**United States (rural) 96%**

**Many of the largest cities in developing world depends  
almost completely on groundwater  
Jakarta, Dhaka, Lima, Mexico City**

# ***Problems Associated with the Use of Groundwater***

- quantities available are limited**
- the rate of groundwater renewal is very slow (the average recycling time 1,400 years)**
- contamination by human activities (pesticides, heavy metals, organic micro-pollutant..)**
- naturally occurring groundwater quality problems (iron, manganese, fluoride, arsenic, boron, methane, ammonium)**

# ***Iron***

- 👁️ **fourth most abundant element on earth crust**
- 👁️ **a common constituent of groundwater  
( 1 to 40 mg/l)**

**No health consequence of iron, taste threshold 0.3 mg/l  
(WHO, 1996)**

## **Problems with iron**

- 👁️ **Staining, coloration, bad taste**
- 👁️ **After growth in the distribution system**
- 👁️ **Incidence of increased turbidity**
- 👁️ **Increased O&M cost for cleaning pipes**

# ***Iron in Groundwater - A Global Problem***

## **Developing Countries (In rural areas)**

- **Rejection of hygienically reliable groundwater because of bad taste**
- **People go back to contaminated sources**

## **Developed Countries**

- **Higher consumer complaints as iron affects household appliances**
- **Increased cost of cleaning pipes (O&M)**
- **Affects further treatment processes**

# ***Iron Removal Methods***

🔗 **Oxidation and Rapid Sand Filtration**

**Oxidation                      O<sub>2</sub> (Aeration)**

**Cl<sub>2</sub>, KMnO<sub>4</sub>, O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, ClO<sub>2</sub>**

🔗 **Limestone Filtration**

🔗 **Oxidising Filters (Manganese green sand)**

🔗 **Stabilization (Sequestering )**

🔗 **Ion Exchange**

🔗 **Sub Surface Removal (Vyredox Method)**

# ***Iron Removal***

## **Standards**

**WHO 0.3 mg/l Guideline value**

**EC 0.05 mg/l Desired , 0.2 mg/l MAC**

**Dutch Water companies <0.03 mg/l (recommendation).**

## **Aeration - Precipitation - Rapid Sand Filtration**

**Most commonly used iron removal method**

- Simple, Economical, No chemicals**

# Oxidation of Iron(II)

## Forms of Iron

 Fe (II) - dissolved ( No oxygen)

 Fe (III) - insoluble ( Oxygen present)

## Oxidation Reaction



1 mg of Fe requires 0.14 mg of oxygen

# Iron Oxidation Kinetics

Stumm & Lee (1961)

$$d [\text{Fe(II)}]/dt = - k p\text{O}_2 \cdot [\text{OH}^-]^2 \cdot [\text{Fe(II)}]$$

$[\text{Fe(II)}]$  = concentration of Fe(II) (mol/l)

$t$  = time (min)

$k$  = reaction rate constant ( $\text{l}^2/\text{mol}^2 \cdot \text{atm} \cdot \text{min}$ )  
=  $1.0 \times 10^{13}$  to  $8.0 \times 10^{13}$

$p\text{O}_2$  = partial pressure of oxygen (atm)

$[\text{OH}^-]$  = concentration of hydroxyl ion (mol/l)

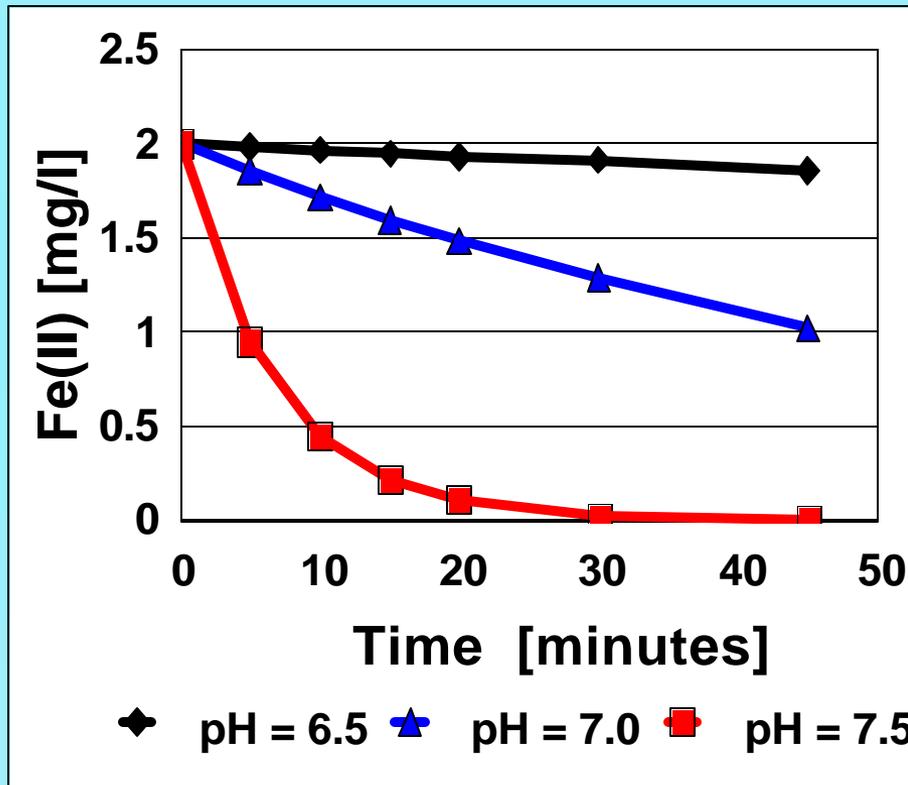
An increase by one pH unit increases oxidation rate 100 fold

Temperature, Alkalinity & Organic matter influence iron oxidation

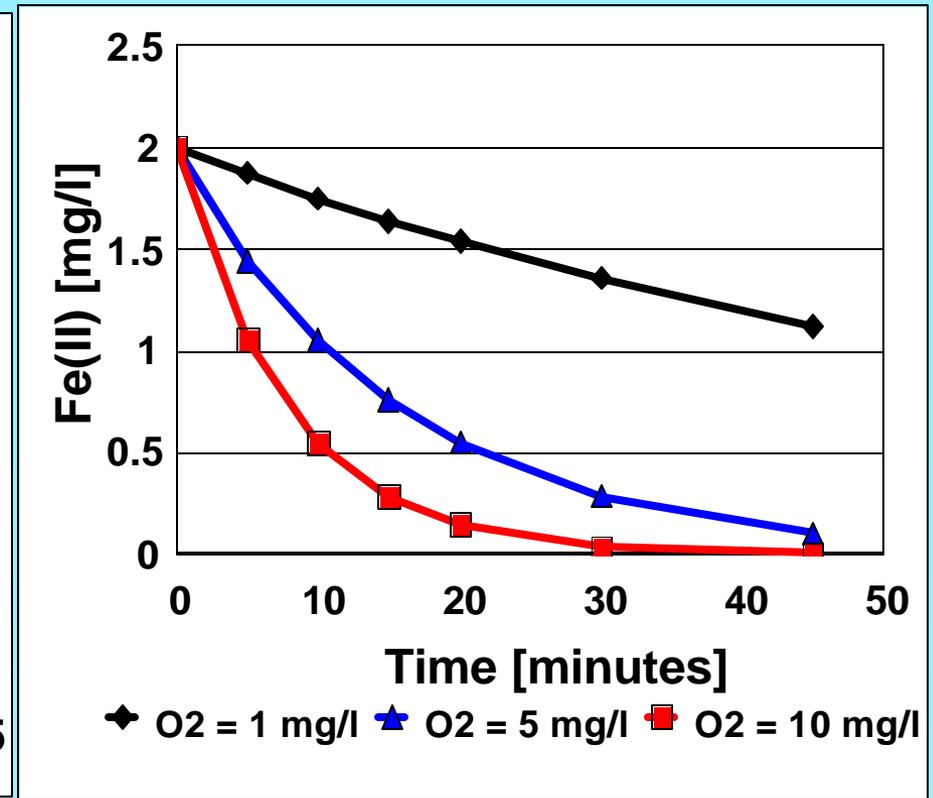
# Sensitivity of Iron Oxidation Kinetics

$$d [\text{Fe(II)}]/dt = - k p\text{O}_2 \cdot [\text{OH}^-]^2 \cdot [\text{Fe(II)}]$$

(Stumm & Lee, 1961)



Effect of pH



Effect of Oxygen

## Example calculation.

What is the initial iron oxidation rate, for an oxygen saturated (25°C) water at pH 7.0 with an initial iron concentration of 5 mg/l.

Oxygen partial pressure

$$= f (P - p_w) / 101\,300 = 0.209(101\,300 - 1\,230) / 101\,300 = 0.21 \text{ atm}$$

$$\text{Fe(II)} = (5 / 1000) / 56 = 8.9 \times 10^{-5} \text{ mol/l}$$

$$[\text{H}^+].[\text{OH}^-] = K_w = 1.01 \times 10^{-14},$$
$$[\text{OH}^-] = 1.01 \times 10^{-14} / 1 \times 10^{-7} = 1.01 \times 10^{-7} \text{ mol/l}$$

Assume  $k = 1.5 \times 10^{13} \text{ l}^2/\text{mol}^2.\text{atm}.\text{min}$

$$\text{Therefore, } d(\text{Fe(II)}) / dt = -1.5 \times 10^{13} \cdot 0.21 \cdot (1.01 \times 10^{-7})^2 \cdot 8.9 \times 10^{-5}$$
$$= -2.86 \times 10^{-6} \text{ mol/min}$$

What is the percentage of Fe(II) remaining after two and twenty minutes?

$$\text{Fe(II)}/\text{Fetot} = \text{EXP}(-k \cdot p_{\text{O}_2} \cdot (\text{OH}^-)^2 \cdot t)$$

at t = 2mins

$$\text{Fe(II)} = 8.9 \times 10^{-5} \cdot \text{EXP} -(1.5 \times 10^{13} \cdot 0.21 \cdot (1.01 \times 10^{-7})^2 \cdot 2) = 8.3 \times 10^{-5}$$

or 93%

at t = 20 mins,

$$\text{Fe(II)} = 8.9 \times 10^{-5} \cdot \text{EXP} -(1.5 \times 10^{13} \cdot 0.21 \cdot (1.01 \times 10^{-7})^2 \cdot 20) = 5.7 \times 10^{-5}$$

or 64%

# ***Reported causes of poor performance of conventional iron removal process***

-  **low oxidation pH**
-  **short time for oxidation**
-  **negative effect of chlorination**
-  **problems related to floc formation**
-  **poor selection of effective sand size**
-  **iron complexation (by silica and humics)**
-  **inappropriate location for reagent dosage**
-  **deterioration of raw water quality over time**

# ***Iron Removal Mechanisms***

**Full understanding of mechanisms involved will help to optimise iron removal process in terms of EFFLUENT QUALITY, PLANT CAPACITY and COSTS**

## **Physical/chemical removal**

 **Oxidation and Floc formation**

 **Adsorption Oxidation Mechanism**

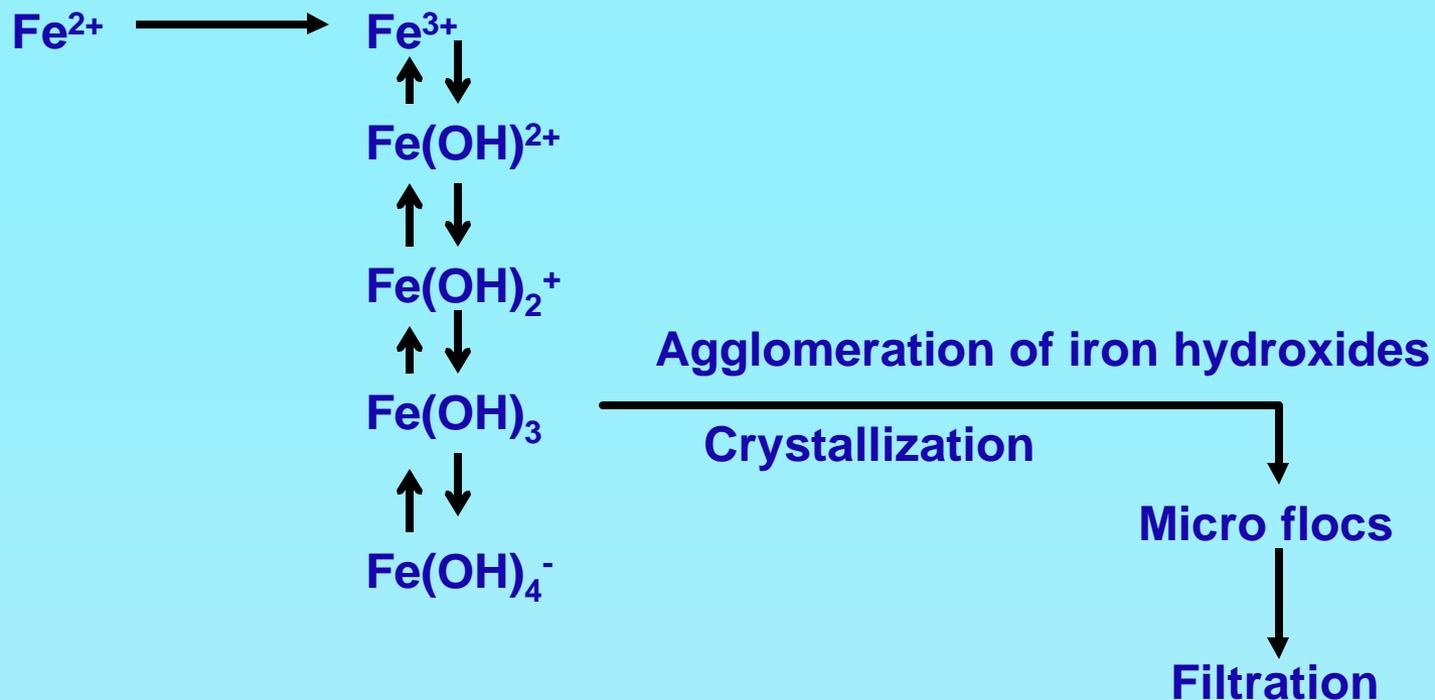
## **Biological Iron Removal**

 **Iron oxidation mediated by “iron bacteria”**

# Oxidation and floc formation mechanism

## Conventional approach

- 🕶 Oxidation of iron(II) to iron(III)
- 🕶 Hydrolysis of iron(III)
- 🕶 Filtration of flocs formed



## ***Problems with floc formation mechanism***

- **Frequent clogging of filters, shorter filter run**
- **Incomplete iron oxidation**
- **Colloidal iron passing through the filter**
- **More sludge treatment and disposal**

# Biological Iron Removal

👁 Oxidation of iron(II) to iron(III) caused by bacteria  
( *Gallionella*, *Crenothrix*, *Sphaerotilus-Lepothrix* )

👁 Bacteria derive energy from the oxidation



👁 Optimum pH 6- 8

👁 Optimum Temperature

10- 15° C (*Gallionella*) , 20 - 25°C (*Spahaerotilus - Lepothrix*)

## Limitations

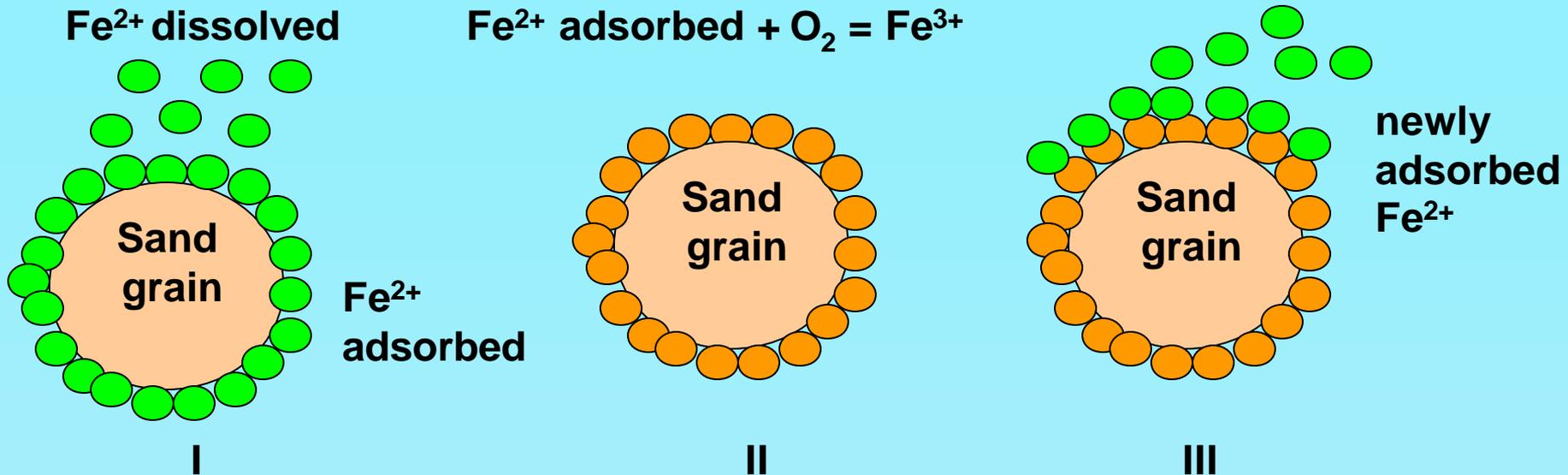
👁 Mechanism not fully understood

👁 Temperature and water quality dependent

👁 pH sensitive

# Adsorption Oxidation mechanism

- 🔗 No pre oxidation of iron(II)
- 🔗 Removal of iron in iron(II) form
- 🔗 iron(II) adsorption onto filter surface/flocs
- 🔗 oxidation of adsorbed iron(II) and creation of new surface for adsorption



# Adsorptive Iron Removal - A Conceptual Model

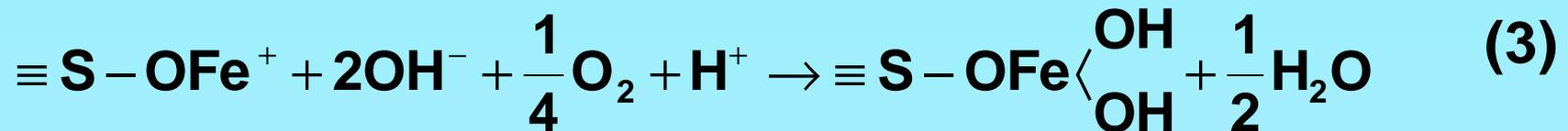
Hydrated surface of filter media



Adsorption of iron(II) onto the surface of filter media



Oxidation of iron(II) & recreation of adsorption sites



# ***Adsorptive Filtration Process***

**Application in water and wastewater treatment increasing**

-  **removal to much lower level**
-  **works over wider pH range**
-  **simultaneous removal of different uncomplexed and complexed metal**
  - iron oxide coated sand adsorbs Cu, Pb, Cd, Ni, As**
-  **low sludge production**

# Adsorptive iron removal

🕒 is the natural process : occurring in the filters of iron removal plant and in sub surface iron removal

🕒 increased efficiency of the filters after the development of coating well known

🕒 Sometimes referred to as “ Catalytic Iron Removal

”

🕒 appropriate for anoxic groundwater

## ***Previous research at IHE on iron removal***

### **Adsorption Oxidation mechanism gives**

- **Lower head loss, longer filter run**
- **Higher removal efficiency**
- **Shorter ripening time**

### ***In addition,***

- **No/less problem of sludge**
- **Reduction in frequency of backwash**

# ***Factors affecting iron removal mechanisms***

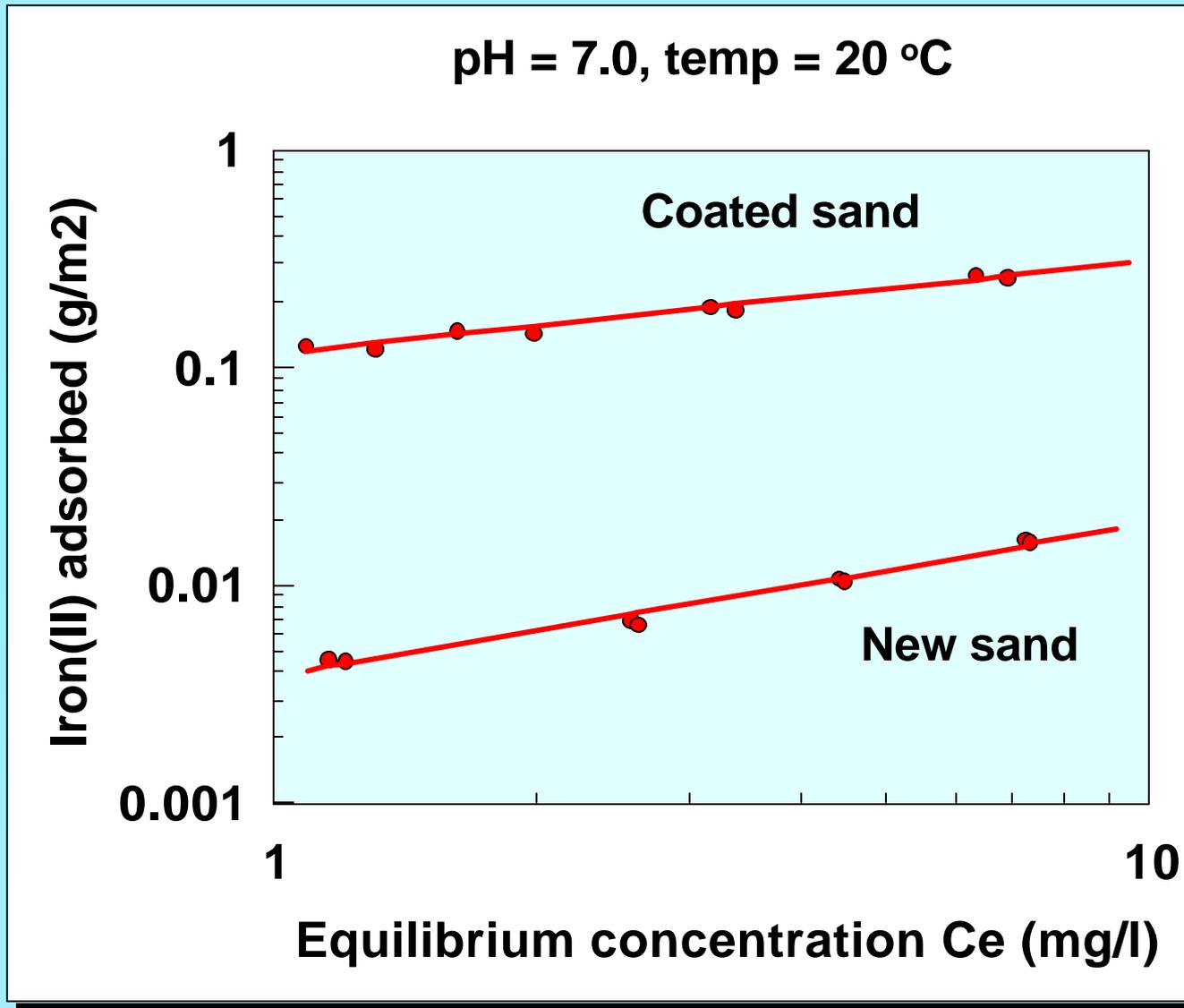
## **A. Water quality parameters**

-  **pH**
-  **Oxygen concentration**
-  **Alkalinity**
-  **Ionic concentration (Mn, Ca, SO<sub>4</sub><sup>2-</sup>)**

## **B. Process conditions**

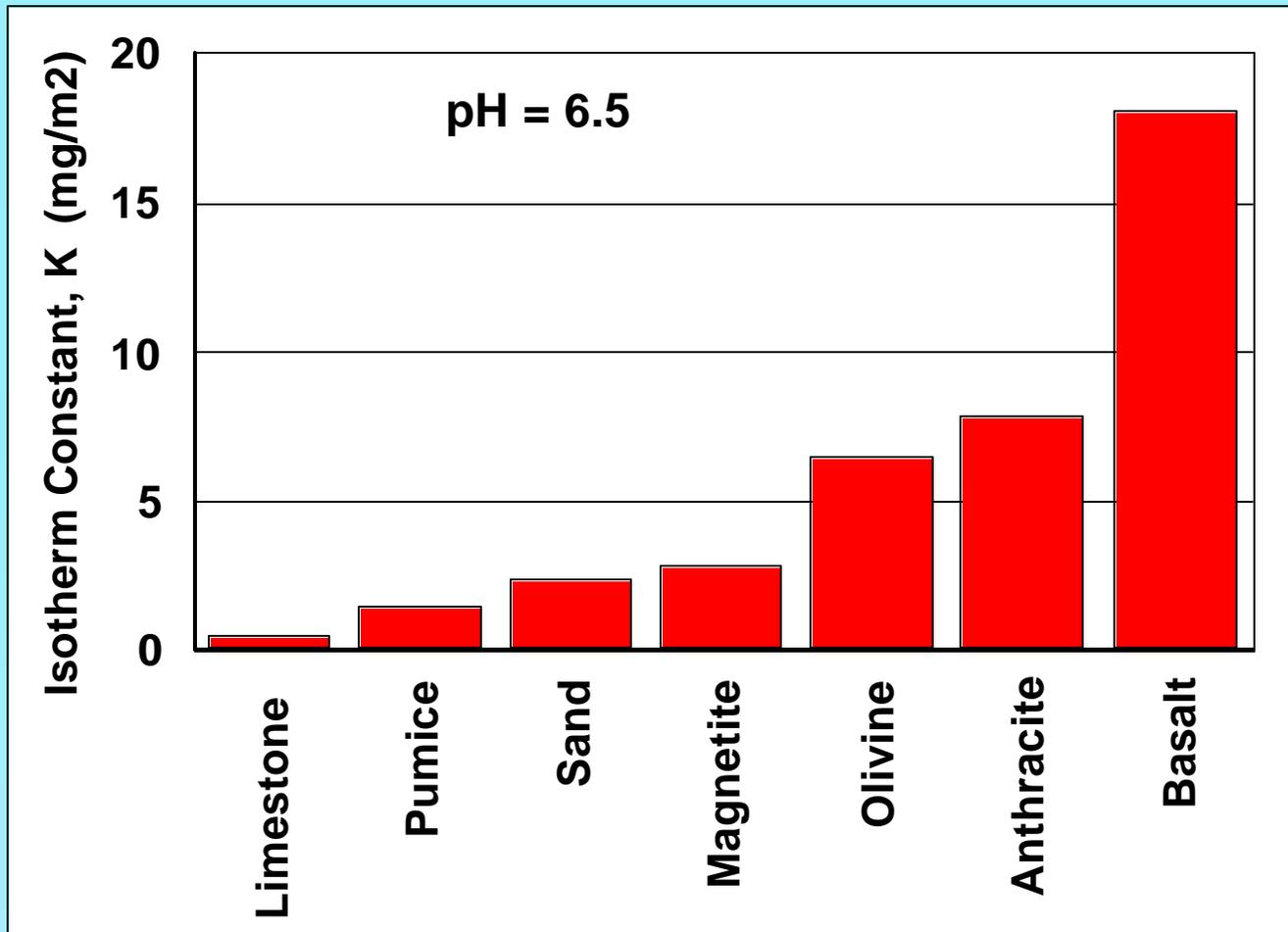
-  **Pre oxidation time**
  - depth of supernatant
-  **Type and size of the filter media**
-  **Age of the filter media**
  - characteristics of the coating

# Iron(II) Adsorption Isotherms



# Adsorption Capacities of Different Filter Media

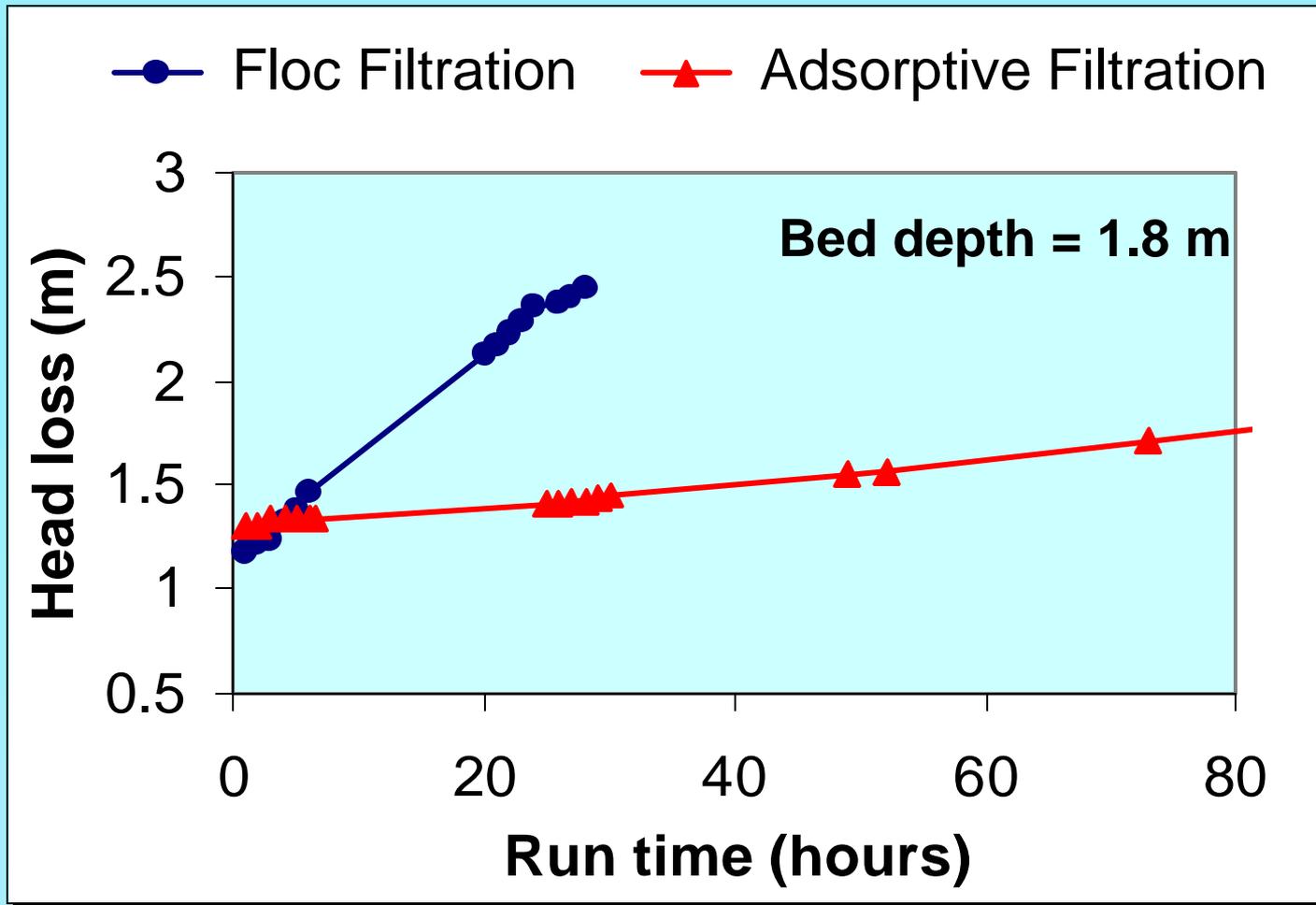
**K** = iron(II) adsorbed per unit surface area ( $Q$  mg/m<sup>2</sup>) at iron(II) equilibrium concentration  $C_e = 1$  mg/l



# Head Loss with Different Mechanisms

Filtration rate = 10 m/h, Depth of supernatant = 1 m

Sand size = 0.5 - 0.8 mm, Influent iron = 1.8 mg/l



# Manganese in Groundwater

Mainly present in GW as  $Mn^{2+}$  (dissolved)

Frequently coexists with  $Fe^{2+}$

- causes similar problems
- taste and staining problems more severe

## Standards

WHO	0.1 mg/l	Guideline value
EC	0.02 mg/l	Desired, 0.05 mg/l MAC

# Manganese Removal

## Oxidation - Rapid Sand Filtration

- Auto catalytic Oxidation

$O_2$ ,  $Cl_2$ ,  $KMnO_4$

Manganese green sand

- Biological Oxidation



1 mg of Mn requires 0.29 mg of oxygen

# Manganese removal

- 👁️ **Rate of oxidation is very slow in solution when pH is less than 8.6**
- 👁️ **In rapid sand filters, oxidation may take place when pH is higher than 7.0**
- 👁️ **The rate of oxidation of  $\text{Mn}^{2+}$  in rapid sand filters is much lower than that of  $\text{Fe}^{2+}$**
- 👁️  **$\text{Mn}_3\text{O}_4$  acts as a catalyst on which  $\text{Mn}^{2+}$  is adsorbed  $\text{Mn}^{2+}$  gets oxidised to  $\text{Mn}_3\text{O}_4$  while older  $\text{Mn}_3\text{O}_4$  gets oxidised to  $\text{MnO}_2$**

# Manganese Removal

Auto catalytic oxidation proceeds as follows



Product of Mn(II) oxygenation are non stoichiometric showing various degree of oxidation ranging from  $\text{MnO}_{1.3}$  to  $\text{MnO}_{1.9}$  (30 to 90% oxidation to  $\text{MnO}_2$ ) under varying alkaline conditions.

# Manganese Oxidation Kinetics

Stumm & Morgan (1981)

$$d [\text{Mn(II)}]/dt = - k'_0 [\text{Mn(II)}] + k'_1 [\text{Mn(II)}][\text{MnO}_2]$$

where  $k' = k p\text{O}_2 \cdot [\text{OH}^-]^2$

$[\text{Mn(II)}]$  = concentration of Mn(II) (mol/l)

$t$  = time (min)

$k_0$  = reaction rate constant ( $\text{l}^2/\text{mol}^2 \cdot \text{atm} \cdot \text{min}$ )

$k_1$  = reaction rate constant ( $\text{l}^3/\text{mol}^3 \cdot \text{atm} \cdot \text{min}$ )

$p\text{O}_2$  = partial pressure of oxygen (atm)

$[\text{OH}^-]$  = concentration of hydroxyl ion (mol/l)

$[\text{MnO}_2]$  = concentration of  $\text{MnO}_2$  on filter media (mol/l)

# Manganese Oxidation Kinetics

Graveland (1975)

$$\frac{d [\text{Mn(II)}]/dt = - k \cdot [\text{Mn(II)}] \cdot [\text{O}_2] \cdot \{[\text{OH}^-] \cdot 10^{-7.0}\} \cdot \{[4.32 \times 10^{-3} + [\text{HCO}_3^-]]\} \cdot \exp(-7000/T) \cdot V_o^{0.35} \cdot d_m^{-1.11}$$

**[Mn(II)] = concentration of Mn(II) (mg/l)**

**t = time (sec)**

**k = reaction rate constant (sec<sup>-1</sup>)**

**[O<sub>2</sub>] = oxygen concentration (mg/l)**

**[OH<sup>-</sup>] = concentration of hydroxyl ion (g/l)**

**[HCO<sub>3</sub><sup>-</sup>] = bicarbonate concentration (mg/l)**

**T = temperature (° Kelvin)**

**V<sub>o</sub> = Filtration rate (cm/sec)**

**d<sub>m</sub> = mean particle diameter (cm)**

# Biological Manganese Removal

- 👓 Oxidation of Mn(II) to Mn(IV) by bacteria  
( *Lepothrix*, *Crenothrix*, *Siderocapsa*, *Mettallogenium*  
*Pseudomonas* )
- 👓 Optimum pH >7.5
- 👓 Oxygen concentration >5.0 mg/l
- 👓 Eh > 300 mv

## Limitations

- 👓 Difficult to control
- 👓 Responsible bacteria require more  
stringent conditions

# Fluoride

## Sources of contamination in drinking water

- dissolution of natural deposits
- discharge from fertilizer and aluminum factories

## Health Effects

**Deficiency - dental caries of children (< 0.5 mg/l)**

**Excess - Skeletal fluorosis**

**pain / tenderness of bones, ligaments become ossified  
and patients become immobilized**

**- Dental fluorosis (mottled teeth)**

**teeth become brittle and break off)**

# Skeletal Fluorosis



# Dental Fluorosis

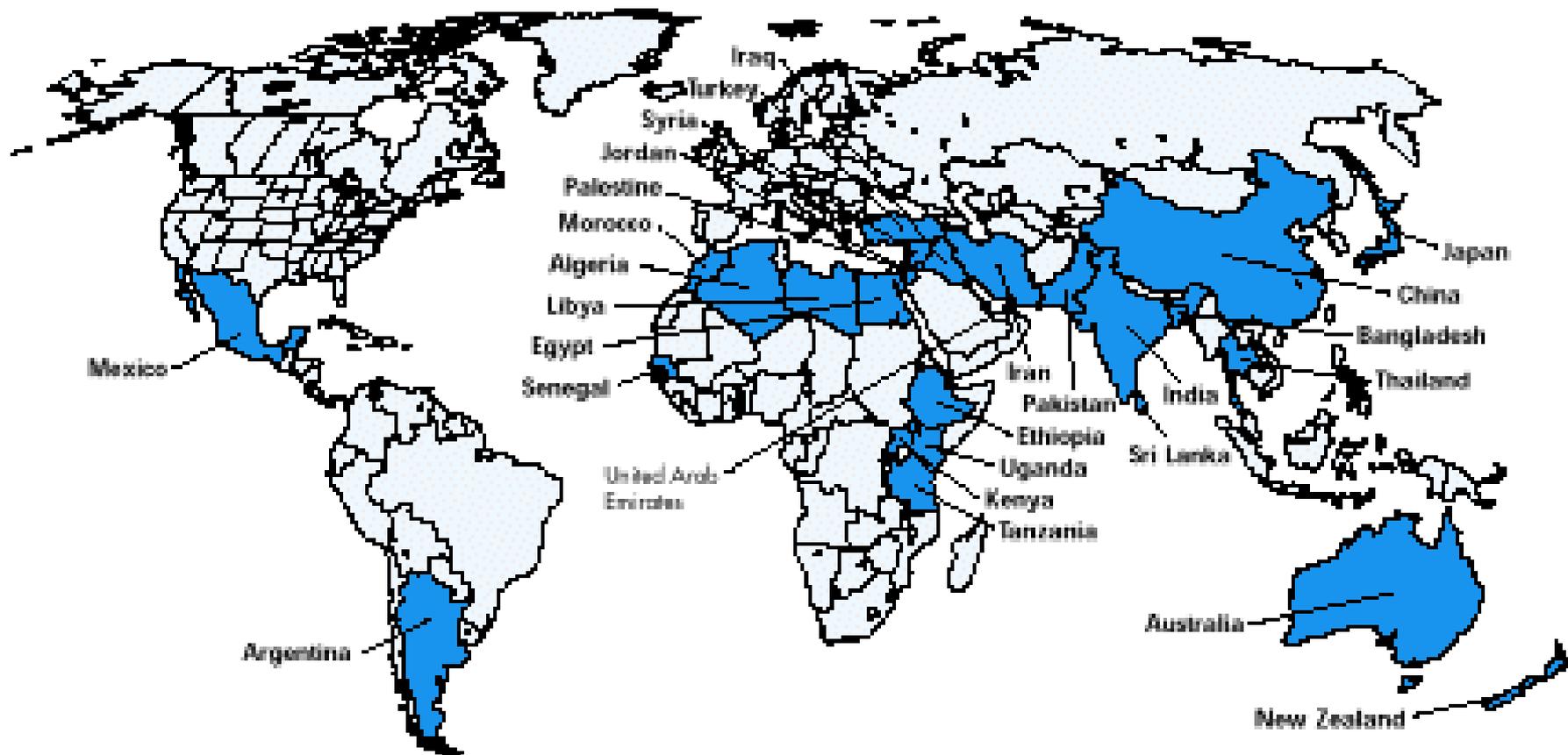


# Fluoride

## Standards

<b>WHO</b>	<b>1.5 mg/l</b>	<b>Guideline value</b>
<b>EC</b>	<b>1.5 mg/l</b>	<b>MAC</b>

# Countries with endemic fluorosis due to excess of fluoride in drinking water



# Fluoride in drinking water worldwide

**Africa:** Ethiopia, Sudan, Kenya, Tanzania, Egypt, South Africa, Nigeria, Senegal, Algeria, Uganda, Zimbabwe, Malawi, Morocco,, and Somalia.

**Asia:** India, China, Korea, Thailand, Sri Lanka, Indonesia, Yemen, and Pakistan.

**Latin America:** Mexico, Peru, Ecuador, Chile, and Argentina.

**Europe:** Greece, Finland, Sweden, Great Britain, Germany, Poland, Moldavia, and Ukraine.

# Fluoride Removal Methods

## 1. Lime and Alum Method ( Nalgonda Technique)

Addition of lime and Al coagulant, followed by flocculation, sedimentation, filtration)

- effective but
- suitable for centralized treatment only,
- requires trained staff, high dosages of Al coagulant,
- high residual aluminum in treated water

## 2. Contact Precipitation

Addition of calcium and phosphate compounds followed by filtration

- very effective,
- new process currently under investigation,
- required chemicals and trained staff

# Fluoride Removal Methods

## 3. Gypsum Filter

Filtration through gypsum filter bed

- effective and inexpensive
- suitable for household level,
- problem: strong increase in calcium & sulfate level

## 4. Adsorption on Bone charcoal

Oldest water defluoridation agent made of animal bones

- used in USA in 40-60s, still used in Thailand and Africa
- ethical, aesthetic, microbiological complains

## 5. Adsorption on Activated Alumina, Ion Exchange, Zeolites)

- under investigation

# Domestic Defluoridation

