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A P P U N T I

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MATERIA: Reclamation of polluted sites - (Esercitazioni) - prof. Zanetti- Ruffino

RECLAMATION OF POLLUTED SITES

esercitazioni

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Practical lesson n. 2 – October 14, 2014 – ENVIRONMENT + PETROLEUM (1.5 h)
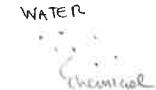
Aqueous solubility is a fundamental, chemical-specific property. It is defined as the concentration of a chemical dissolved in water when that water is both in contact and at equilibrium with the pure chemical. (For the moment consider the chemical to be in either liquid or solid form). Although aqueous solubility is temperature dependent, it does not vary greatly for a given chemical over the typical range of temperatures encountered in the environment.
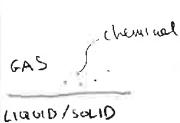
Vapor pressure, another chemical-specific property, is defined as the partial pressure of a chemical in a gas phase that is in equilibrium with the pure liquid or solid chemical. For example, if at 20°C a bottle contains both air and pure liquid TCE, the partial pressure of TCE vapor in the air-filled neck of the bottle (the headspace) will be approximately 0.08 atm (61 mmHg), which corresponds to 0.0033 mol/l (440 mg/l). The ideal gas law is used to convert the vapor pressure into the corresponding moles of vapor per unit volume:

$$\left(\frac{n}{V}\right) = \frac{P}{RT}$$

1. Soil venting – toluene, xylene, maximum concentration in the gas phase
A soil is contaminated by a mixture of toluene (50% b.w.) and xylene (50% b.w.). The selected reclamation technique was SOIL VENTING, performed at 20°C. What is the maximum concentration (mg/m^3) of the two contaminants in the extractable vapor?
Toluene: vapor pressure, 22 mmHg; molecular weight, 92.1 g/mol
Xylene: vapor pressure, 10 mmHg; molecular weight, 106.2 g/mol

Henry's law constant - definition

2. How many grams of carbon dioxide gas is dissolved in a 1 L bottle of carbonated water if the manufacturer uses a pressure of 2.4 atm in the bottling process at 25°C? Given H of CO_2 in water = 29.76 atm/(mol/L) at 25°C.

3. Consider an unsaturated soil. Suppose the concentration of dissolved oxygen in soil water at equilibrium with soil air is 100 µmol/l (µM). Given an Henry's law constant of 26 (H*, dimensionless) for oxygen at 20°C, what is the corresponding oxygen concentration in the soil air? What is the Henry's law constant in units of $atm \cdot m^3/mol$ at 20°C?

4. If 10 mg of naphthalene is added to 1 liter of water in a 20-liter sealed bottle (the solubility of naphthalene is $2.6 \cdot 10^{-4}$ mol/l and the vapor pressure is $3 \cdot 10^{-4}$ atm a 20°C):
• What is the dimensionless Henry's law constant?
• What percentage of the total naphthalene ends up in the air-filled volume of the bottle at equilibrium?

Practical lesson n. 5 – November 4, 2014

1. OC – Water partition

The suspended solid content (Css) of a 1-liter river water sample is 20 mg.

Assume this material is all organic carbon and that K_{OC}, the organic carbon – water partition coefficient for a chemical of interest, is approximately 4000 l/kg.

A laboratory filters the sample before analysis, analyzing the filtrate (water that does pass through the filter) and reporting the chemical concentration, Cw, of the filtrate.

If the sample had not been filtered, how much of this chemical would have been measured (Ct)?

Express in terms of the measured concentration Cw (mg/l) of the filtered sample.

2. Estimation of the retardation factor, R

For an aquifer with a bulk density of 2 g/cm^3 containing 0.5% (b.w.) organic carbon, estimate the retardation factor for the common polycyclic aromatic hydrocarbon (PAH) naphthalene ($C_{10}H_8$). If the porosity of the aquifer is 0.24, the hydraulic conductivity is 10^{-3} cm/s and the hydraulic gradient is 0.001, how fast will a plume of naphthalene travel?

3. Adsorption on activated carbon

A groundwater is contaminated by an amount of toluene equal to 5 mg/l. The toluene concentration has to be lowered from 5 mg/l to 100 mg/l.   ^μg/l

A in-situ adsorption on granular activated carbon (GAC) was chosen as a remediation technique.

Do the calculation of the GAC total capacity and of the exhaustion time.

PROBLEM DATA

Aquifer flow rate, $Q = 2.0 \cdot 10^{-3}$ m^3/s

Seepage velocity, $v = 3.4 \cdot 10^{-3}$ m/s

Contact time between water and GAC, CT = 12 min

GAC density, $\rho_{GAC} = 480$ kg/m^3

GAC adsorption capacity, $S_{GAC} = 0.01$ kg/kg

Height of the GAC bed, H = 0.91 m

Diameter of the GAC bed, D = 0.46 m

Volume of GAC in each tank, V = 0.151 m^3

4. Evaluation of the mass and volume of the free product

A sample campaign in a contaminated site revealed that the free product was widespread on a rectangular area, 15.24 m long and 12.19 m wide.

The actual thickness of the free product in four piezometers located in the area is shown in the picture. The soil porosity (n) is equal to 0.35.

The density of the contaminant (ρ_c) is equal to 0.8 g/cm^3.

QUESTION: how much is the volume and the mass of the free contaminant in the subsurface?

Practical lesson 7 – November 24, 2014 (1.5 hours)

Table 13.3	Summary of the Kinetics of Zero-Order, First-Order, and Second-Order Reactions		
Order	Rate Law	Concentration-Time Equation	Half-Life
0	Rate $= k$	$[A]_t = -kt + [A]_0$	$\dfrac{[A]_0}{2k}$
1	Rate $= k[A]$	$\ln\dfrac{[A]_t}{[A]_0} = -kt$	$\dfrac{0.693}{k}$
2†	Rate $= k[A]^2$	$\dfrac{1}{[A]_t} = kt + \dfrac{1}{[A]_0}$	$\dfrac{1}{k[A]_0}$

†A $\longrightarrow$ product.

1. A sealed radioactive source used for physics demonstrations in 1940 contained 10 microcuries (μCi) of ^{60}Co (cobalt-60). Given a half-life of 1900 days for ^{60}Co, what would be the source strength in 2014?

2. Spilled benzene (C_6H_6) dissolves into a river flowing at an average velocity of 0.3 m/s. Will biodegradation significantly decrease the concentration of benzene in the river over a 20-mi reach?
An approximate aerobic degradation rate for benzene is 0.11/day. Assume first order decay.

3. Benzo[a]pyrene is measured in a facility wastewater lagoon 2.5 h after a release at a concentration of 3 μg/l. If direct photodegradation is the only degradation process occurring, what was the initial concentration of B[a]p in the lagoon?
PAH such as B[a]p are likely to directly photodegrade because double bond in aromatic rings can absorb light. An approximate half-life for B[a]p due to direct photodegradation is 1 h.

4. Anaerobic bacteria living at the bottom of a shallow inlet to a salt marsh are generating hydrogen sulfide (H_2S) as a by-product of their metabolism. Although this compound (which is responsible for the "rotten egg" smell characteristic of salt marshes and is extremely toxic) is ordinarily found as a gas, it is reasonably soluble in water. What is the maximum concentration of dissolved hydrogen sulfide species (including H_2S, HS^- and S^{2-}) that could theoretically accumulate in the waters of the inlet if the pH is 6.0? (this absolute limit would be reached when the pressure of H_2S reached 1 atm and bubbles of pure H_2S formed and escaped. In practice, H_2S concentrations would typically be lower). Some relevant equilibria include:

$H_2S \Leftrightarrow H_2S(g)$	$H = 10^{0.99}$ atm·liter/mol
$H_2S \Leftrightarrow H^+ + HS^-$	$K = 10^{-7.02}$ M
$HS^- \Leftrightarrow H^+ + S^{2-}$	$K = 10^{-13.9}$ M

A small amount of dibromomethane (CH_2Br_2) has been spilled into the described inlet. Assume that the partial pressure of H_2S is 0.1 atm. If the principal process that will affect the fate of this species is its reaction with HS^-, for which the relevant rate constant is **$5.25 \cdot 10^{-5}$ M^{-1} s^{-1}** (note that other dissolved hydrogen sulfide species do not react at measurable rates), how many days will be required for the CH_2Br_2 concentration to decrease to 10% of its initial value?

[handwritten note:] this environment contains some electron acceptor typical of the aerobic and anoxic environment

[handwritten note:] we have to transform this environment in an anaerobic environment (we have to consume all the electron acceptor species)

Table 1.1. Concentrations of redox sensitive species in groundwater at the site in the core of the plume, downgradient and in a background well.

[handwritten note: aerobic environment]

	Background well	Well in the core of the plume	Well downgradient the source
	mg/l	mg/l	
O_2	1.6	1.7	1.4
NO_3^-	32	31	25
Mn(II)	0.01	0.02	0.01
Fe(II)	0.2	0.15	0.25
SO_4^{2-}	62	59	72
CH_4	below detection limit	below detection limit	below detection limit

[handwritten notes: metalli in forma ridotta; electron acceptors typical of aerobic environ.; metallo in forma ossidata]

Table 1.2. Reaction schemes for degradation of ethanol.

Process	Reaction
O_2 respiration	$3\ O_2 + C_2H_6O \rightarrow 2CO_2 + 3H_2O$
NO_3^--red.	$6\ NO_3^- + 2.5\ C_2H_6O + 6H^+ \rightarrow 5CO_2 + 10.5\ H_2O + 3N_2$
Fe(III)-red.	$6\ Fe^{3+} (s) + 0.5\ C_2H_6O + 1.5\ H_2O \rightarrow 6\ Fe^{++} + 6H^+ + CO_2$
SO_4^{2-}-red.	$6SO_4^- + 4\ C_2H_6O + 12H^+ \rightarrow 6\ H_2S + 8\ CO_2 + 12H_2O$

The dimensions of the column are as follows:

Length, L = 50cm
Internal diameter, D = 3cm

The distances, h₁ and h₂ shown on Figure 2 is:

h₁ = 20cm
h₂ = 50cm

The following parameters for the iron are obtained from the manufacturer:

Porosity, ε = 0.55
Bulk density, ρ_B = 3 kg/l → densità del ZVI nella colonna

Question 1
The first experiment showed that a water flow through the column of Q= 0.02 l/min is obtained.
Calculate the hydraulic conductivity of the Conelly iron.

$$\text{DARCY} \quad K = \frac{Q \cdot L}{\frac{\pi}{4} D^2 \cdot h_2}$$

→ permeabilità

The second experiment determined a half-life for the 1. order degradation of TCE and DCE of 2 h and 7 h, respectively. The third experiments showed that the breakthrough of chromate at the effluent of the column first appeared after 400 pore volumes of water has passed the column. The inlet concentration in this experiment was 20mgCr/l. The fourth experiment showed that the degradation of TCE and DCE was insignificant in the column after chromate breakthrough.

Question 2
Calculate the chromate reduction capacity (in gCr/kg ZVI).

1) calcolo volume pori
$$P_V = \varepsilon \cdot V_c \quad (\text{volume colonna})$$
$$P_V = \varepsilon \cdot \frac{\pi}{4} D^2 \cdot L$$

2) MASSA Cr Rimossa
$$M = 400 \cdot P_V \cdot C$$
$$M = V_c$$

3) MASSA DI ZVI in colonna
$$M_{ZVI} = \rho_B \cdot V$$

→ concentrazione r. di fe in ingresso
→ volume di H₂O trovato nella colonna

$$\Rightarrow CRC = \frac{M}{M_{ZVI}}$$

From pump tests carried out in the aquifer, the hydraulic conductivity of the aquifer was determined to 8·10⁻⁴ m/s. The head difference between well MW1 and MW2 was measured to 20 cm. The distance between the two wells is 100 m. The porosity of the aquifer material is 0.3.

Question 3
Will a continuous PRB as wide as the plume and keyed into the underlying clay layer treat the whole plume?

confronto tra: K_{aq} | cfr | $K_{barriera}$

barriera efficace $K \geq K_{aq}$
→ altrimenti il H₂O passa intorno

Question 4
Dimension the PRB using the parameters determined in the lab tests. The PRB should be able to contain all chromate originating from both the soil and the aquifer, and to meet the MCLs for both TCE and DCE at the downstream side of the PRB. The pore water velocity in the PRB is assumed to be equal to the velocity in the aquifer. It is assumed that the chromate is leached out of the soil and aquifer much faster than the chlorinated compounds.

→ calcolo dei 3 spessori:

1) cromo:
$$\frac{\text{massa tot } M_{Cr}}{mm} = (H \cdot L_1 \cdot \rho_b \cdot C_S + \varepsilon H \cdot L_2 \cdot C_w)$$
equilibrio

$$L_{PRB1} = \frac{M_{ZVI}}{H_1 \cdot \rho_b}$$

$$\frac{\text{massa tot}}{mm} \quad M = \frac{M_{Cr}}{CRC}$$

2) TCE DCE:
$$\ln C = \ln C_0 - kt \rightarrow \ln \frac{C_0}{C} = kt$$
$$t = \frac{1}{k} \cdot \ln \frac{C_0}{C}$$

→ tempo x completo
$$t = \frac{L_{PRB2}}{v_p} \rightarrow L_{PRB2} = v_p \cdot t = v_p \cdot \frac{1}{k} \cdot \ln \frac{C_0}{C}$$

la ricavo da $t_{1/2}$: $k = \frac{\ln 2}{t_{1/2}}$

$$L_{PRB2} = \frac{t_{1/2} \cdot v_p}{\ln 2} \cdot \ln \left(\frac{C_0}{C} \right)$$

3

13/10/2014

ESERCITAZIONI RECLAMATION

Esercitazione 1

ES.1) AIR SAMPLE

$$p = 1 \text{ atm}$$
$$\rho = 1,3 \text{ g/l}$$
$$SO_2 = 25 \text{ } \mu g/m^3$$

$\dfrac{mg \, SO_2}{10^6 \, mg \, air} \rightarrow 1 \, kg$

1) ppm b.w. (by weight) $\dfrac{mg \, of \, contaminant}{1 \, kg \, of \, air}$

2) moles SO_2 per 10^6 mol of air

$1 l = 1 dm^3$
$1 l = 10^{-3} m^3$

Risoluzione :

1) $\dfrac{0.025 \text{ mg } SO_2}{1,3 \text{ kg air}}$

$1 m^3$ aria $\rightarrow 1,3 \text{ kg/m}^3$

because $M = V \cdot \rho = 1 m^3 \cdot 1,3 \dfrac{kg}{m^3} = 1,3 \, kg$

$\dfrac{1,3 \, g}{10^{-3} m^3} \rightarrow \dfrac{1,3 \cdot 10^{-3} kg}{10^{-3} m^3}$

$$0,025 : 1,3 = X : 1 \qquad \boxed{X} = 19,2 \cdot 10^{-3} \text{ ppm} \quad \left[\dfrac{mg}{1 Kg}\right]$$

2) $25 \text{ } \mu g/(m^3) \rightarrow 0,39 \cdot 10^{-6} \text{ mol } SO_2$

$16 \cdot 2 + 32$

$MW(SO_2) = 64.06 \text{ g/mol}$

$\underset{32}{} \quad \underset{16}{}$

$mol = W/MW = 25 \cdot 10^{-6} g / 64,06 \dfrac{g}{mol}$
$= 0,39 \cdot 10^{-6} \text{ mol}$

in $1 m^3$ di aria

$1 m^3$

$$P V = \boxed{M} R T$$

$R = 0,082 \dfrac{atm \cdot l}{mol \cdot K}$

1 atm

$1 m^3$
$1000 l$

HP:
$T = 273 K \rightarrow$ a 9st T HP che si abbia 9st densità $\rho = 1,3 \text{ g/l}$
$0°C$

$m = 44,6 \dfrac{mol}{of \, air} \qquad m = \dfrac{PV}{RT}$

$0,39 \cdot 10^{-6} \text{ mol } SO_2 / 44,6 \text{ mol air}$

$$0,39 \cdot 10^{-6} : \boxed{44,6} = X : \boxed{10^6} \qquad \boxed{X} = 8,74 \cdot 10^{-3} \text{ ppm (b.v.)}$$

mol of air

+ è utile trovare dati conist unità di misura

ES.2)

$C_0 = 0$
INFLOW   PIPE   → OUTFLOW

$C_0 = 10^{-4} \dfrac{kg}{m^3}$

$Q = 3 \cdot 10^6 \text{ } m^3/d$

$\dot{M}_{tot} = 20 \text{ kg/d}$

the max flow rate at which butanol enter in the lake

How much butanol disappear from the lake

$Q \cdot C$

INTERNAL SINK RATE $(kg/d) = 20\dfrac{kg}{d} + 0 - 3 \cdot 10^6 \dfrac{m^3}{d} \cdot 10^{-4} \dfrac{kg}{m^3}$

pipe

$3 kg/d$

$= 17 \dfrac{kg}{d}$ volatilization, biodegradate

amount of butanol that leave the system by the outflow

$$M_b = 6 \cdot 10^3 \frac{mol}{\ell \cdot d} \cdot 133,4 \frac{Mg}{mol} \cdot 6818 \cdot 10^3 \ell \cdot \frac{1}{1440} \frac{d}{mm} \cdot 1 \ mm$$

peso molecolare

volume aria

$$= 3790 \ \mu g = 3,79 \ mg$$

$$M_{OUT} = 415,3 \ \frac{mg}{mm}$$

$$M_{in} \left[\frac{mg}{mm}\right] = \cdot C_m \left[\frac{mg}{\ell}\right] \cdot Q_m \left[\frac{\ell}{mm}\right]$$

$$C_m \simeq 457 \ \frac{\mu g}{\ell}$$

$$C_m = \frac{M_{in}}{Q_m} \left[\frac{mg}{\ell}\right] = 0,457 \ \frac{mg}{\ell}$$

14/10/2014
Esercitazione 2

ES.1)

for ex:
1000 g
- 500 g T
- 500 g X

We can refer to any other but the ratio of mass between the 2 cont must be 1:1

$\frac{1}{1}$ ratio T-X by weight in soil

SOIL

What is the concentration in this air stream?

C_T C_X

T   X

AIR

SOIL VENTING technique

TOLUENE

CH_3

XYLENE

CH_3 CH_3

Molecular weight (from the formula)

$MW = 92,1 \ \frac{g}{mol}$
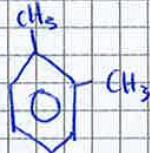
$MW = 106,2 \ \frac{g}{mol}$

$P_T = 22 \ mmHg$

$P_X = 10 \ mmHg$

Molar fraction - soil

1000 g

500 g T / 92,1 = 5,43 mol
500 g X / 106,2 = 4,71 mol

$$T = \frac{5,43}{5,43 + 4,71} = 0,54 \rightarrow \text{molar fraction } T \text{ in soil}$$

$\frac{5}{5} \rightarrow$ ratio T-X in soil

$$X = 1 - T = 1 - 0,54 = 0,46 \rightarrow \text{molar fraction } X \text{ in soil}$$
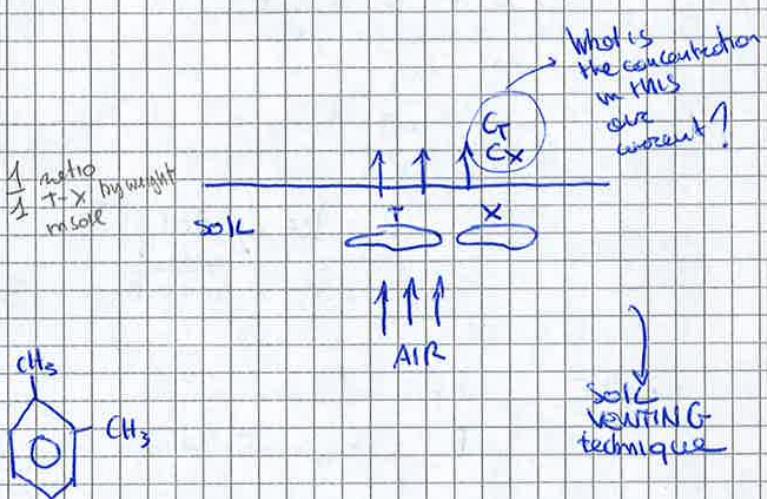
ratio between T and X in AIR FLOW :

$$T = \frac{59,3}{59,3 + 26,9} = 0,69$$

↳ g of T in 1 m³

ratio of the total amount of T released to the total amount of contaminant

$$\frac{7}{3}$$ → ratio by weight
T - X
mor

$$X = \dots = 0,31$$

— — — — — — — — — — — — — —

Henry constant

→ perchè non pressione parziale?

$$H = \frac{\text{Vapor pressure } [\text{atm}]}{\text{water solubility } [\frac{mol}{\ell}]} = \left[\frac{\text{atm} \cdot \ell}{\text{mol}}\right]$$

a T costante la quantità di un gas disciolto in un dato volume di liquido è proporzionale alla press. del gas nella fase gassosa sovrastante la soluzione

↓

we have a ratio between 2 imp. properties of 2 substances

NB Water and air in equilibrium

$$\boxed{\text{TOLUENE}}$$ $$\boxed{P_T}$$ AIR

in contact with pure phase of air

eq. betw. pure phase and air and the equilibrium is = vapour concentration pressure

conc. of T we have in the air in equilibrium with the pure phase

→ f(T)

$$\boxed{\text{TOLUENE}}$$ $$\bigcirc \text{WATER ST}$$

pure phase ʃ water in contact with

eq. between pure phase and water and the equilibr. conc. is = WATER solubility

conc. of T in water in equilibrium with the pure phase

$$H^* = \frac{H}{R \, \bigcirc T}$$

↳ temp. value at which I calculate H constant

AIR ‾‾‾ $\frac{mg}{\ell \, air}$
WATER ‾‾‾ $\frac{mg}{\ell \, H_2O}$
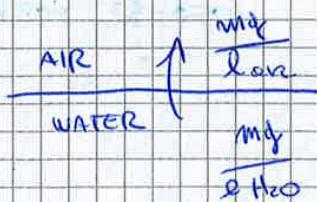
to pass from the same measure unit but in 7 media I use H*

pressione di vapore = pressione parziale all'equilibrio

$$H = H^* \cdot R \cdot T = 26 \cdot 0,0821 \; \frac{l \cdot atm}{mol \cdot K} \cdot 293K \rightarrow 625 \; \frac{l \cdot atm}{mol}$$

$$= 0,625 \; \frac{atm \cdot m^3}{mol}$$

ES.9)

↓ 10 mg meoh

20 l

12 l AIR
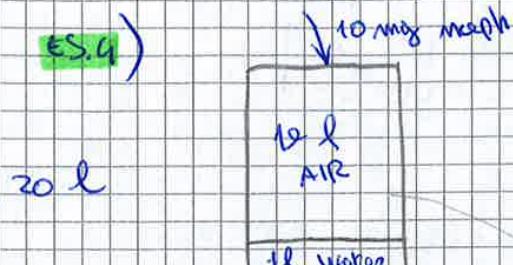
1l water

$$S_w (20°C) = 2,6 \cdot 10^{-4} \; \frac{mol}{l}$$

$$P (20°C) = 3 \cdot 10^{-4} \; atm$$

• $$H = \frac{P}{S} = \frac{3 \cdot 10^{-4} \; atm}{26 \cdot 10^{-4} \; \frac{mol}{l}} = 1,15 \; \frac{atm \cdot l}{mol^{-1}}$$

$$H^* = \frac{H}{RT} = 4,79 \cdot 10^{-2}$$

• % meoh in the air   the amount of meoh in this part

% meoh in the air = $\frac{mol \; meoh \; air}{mol \; air + mol \; water}$ → volume of the air [l]

conc. in the air $\left[\frac{mol}{l}\right]$ = $\frac{C_a \cdot V_a}{C_a \cdot V_a + C_w V_w}$ = $\frac{C_w H^* \cdot V_a}{C_w H^* V_a + C_w V_w}$ = $0,477$ $\frac{4,8 \, mm^3}{10 \, l}$ 48%

0,75 $\frac{mm^3}{l}$

because $C_a = H^* \cdot \boxed{C_w}$

↓ we don't know this term but wee can eliminate this

52% in water

$C = \frac{5 \, mg}{l}$

ES. 2) $u_{10} = 4 \, m/s$

$K_e = 1,1 \, cm/s$

$0,3 + 0,2 \cdot 4$

$$c_g = \frac{P \cdot M_w}{RT} = 0,151 \frac{mg}{cm^3}$$

$> 0,0328 \, atm$

$\phi = K_e \cdot c_g = 0,17 \frac{mg}{cm^2 \cdot s}$

$mol \cdot \frac{g}{mol}$

114

Mass of 2,2,4 TMP = $10 \, \ell \cdot 7 \frac{mol}{\ell} = 70 \, mol = 7980 \, g$

$$\frac{M}{cm^2} \quad \frac{7980 \, g}{210\,000 \, cm^2} = 0,038 \frac{g}{cm^2} = 38 \frac{mg}{cm^2}$$

$21 \, m^2$

$$\frac{38 \, mg/cm^2}{0,17 \frac{mg}{cm^2 \cdot s}} \cong 230 \, s$$

$1 \, atm = 760 \, mmHg$

ES. 3) $u_{10} \rightarrow$

$u_{10} = 4,5 \frac{m}{s}$

Chlorobenzene C_6H_5Cl
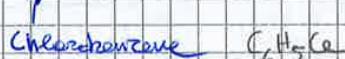
is the same
of 1) $K_A = 1,2 \, cm/s$

$p = 1,6 \cdot 10^{-2} \, atm$

da formula di
Clorobenzene $M_w = 112,56 \frac{g}{mol}$

$$c_g = \frac{P \cdot M_w}{RT} = 7,49 \cdot 10^{-2} \quad g/\ell \text{ or } mg/cm^3$$

$$\phi = K_e \cdot c_g = 8,98 \cdot 10^{-2} \frac{mg}{cm^2 \cdot s}$$

H_2O e aria in eq.
uso legge di
H se conc. + tens.
interfase vale.

water

Clorob. e H_2O
in eq. $\Rightarrow$ conc = solubilità
interfase

clorobenzene
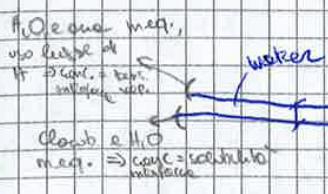
1 cm

equilibrio tra:
fase pura, H_2O, atm

1° equil. fase
pura - H_2O $\Rightarrow$ $S = 472 \frac{mg}{\ell}$ = conc. massima strato   (perché all'equilibrio)

2° equil.
fase H_2O
-
atm : $$H = \frac{P}{S} \rightarrow$$ tens. di vapore

non so quanto vale

is the same value must
I have between
pure phase + atm
$CH_2 \rightarrow$ atm

mi viene
la stessa c_g
e quindi
stesso ϕ

$\frac{P \cdot M_W}{RT}$

dov'è l'errore?

non è corretto usare
però la stessa K_A

$K_e = a + b \, u_{10}$

vuoto pure vale
solo se c'è
contatto tra
sost. pura e aria

762

$\downarrow$

749,3   la press.
è diminuita

volume $\rightarrow$ V
35 l
(half of 70)

We can calculate: conc. spazio di testa

$M = V \cdot C$

$35\, l \cdot 7,1 \cdot 10^{-2}\, \frac{g}{l}$ a P = 762
spazio
di testa

= 2,5 g octane nello
spazio di testa

$\frac{749,3}{762} \cdot 100 = 98,3\%$ diminuz. %
di pressione

$1,7\% \cdot 2,5g = 0,041 g$

massa
che c'era
prima

massa
che abbiamo
perso

se V diminuisce anche
la massa di contaminante|,

$H = \frac{P \downarrow}{S \downarrow}$

se P scende anche
S scende (H cost)

$S = K_{ow} \cdot C_L$ conc. in the
liquid phase $\left[\frac{mg}{kg\,water}\right]$, ppm

octanol water partition
coefficient

$\left[\frac{kg\,water}{kg\,octanol}\right]$ usually
is given
without
dimension $[-]$

conc. in
the octanol
phase

$\left[\frac{mg}{kg\,octanol}\right]$, ppm

ES 1)   lake conbaminated   with

OH

CH₃

meta-cresol
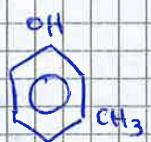
concentration in
fishes (in the fatty tissues)

$S = 0,1$ ppm

What is C_L?

$MW = 108,14 \quad g/mol$

$S_{H_2O} = 2780 \; mg/l \; (\approx 20°C) \rightarrow$ max value
of C_L

$\log K_{ow} = 1,96 \quad \rightarrow K_{ow} = 91,2$

$C_L = \frac{S}{K_{ow}} = 1,10 \cdot 10^{-3}$ ppm

ES.2) AIR $\rightarrow$ | 50 ml

OCTANOL $\rightarrow$ | 200 ml

WATER $\rightarrow$ | 250 ml
5.0 mols
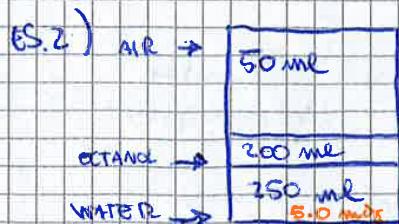
We add an amount of orto-xylene

CH₃

CH₃
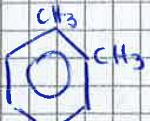
after a certain
time is in equil.
with the other phase

what is the total
amount of o-xylene ?

ES.2)

c_L 5 mg

$$S = k_{ow} \cdot \boxed{C_L} = 26 \cdot 365 \; \frac{mg}{kg}$$

$$\frac{5.0 \, mg}{250 \, ml} = 0,02 \; \frac{mg}{\boxed{ml}} = 20 \; \frac{mg}{kg}$$

$$1 \, ml = 10^{-3} \, kg$$
$$1000 \, ml = \boxed{1 \, kg}$$

$$26 \cdot 365 \; \frac{mg}{\boxed{1 \, kg}} \cdot \rho_{oct} = 21 \cdot 751 \; \frac{mg}{dm^3}$$

$$\rightarrow \; 21 \cdot 751 \; \frac{mg}{l} \cdot 0{,}0200 \, l = \boxed{4 \cdot 350 \, mg}$$

$$m = \rho \; \left[\frac{kg}{m^3} \right] \qquad \frac{kg}{m^3} \qquad V \qquad m^3$$

$$\rho = \frac{m}{V} \quad \rightarrow \quad V = \frac{m}{\rho}$$

$$C_a = H^* \boxed{C_w} = 2{,}2 \cdot 10^1 \cdot 0{,}02 \; \frac{mg}{ml} = 0{,}0044 \; \frac{mg}{ml} \cdot 50 \, ml$$

$$= \boxed{0{,}22 \, mg}$$

$$1 \, ml =$$
$$1000 \, ml = 1 \, kg$$

$$M_{TOT} = 5 + 4350 + 0{,}22 = 4355{,}22 \, mg$$

$$M_s = \boxed{f_{oc} \cdot K_{oc}} \; C_w \, C_{ss} \, V$$

C_s K_d

→ all the soil is made by organic carbon $f_{oc} = 1$

$$C_t \cdot V = C_w \cdot V + \boxed{f_{oc}} \, K_{oc} \, C_w \, C_{ss} \, V$$

$$C_t = C_w \left(1 + 1 \cdot 4'000 \, \frac{l}{kg} \cdot 20 \, \frac{mg}{l} \cdot \frac{kg}{10^6 mg} \right) = 1,08 \, C_w$$

ES.2)

$$\boxed{R = 1 + K_d \cdot \frac{\rho_b}{m}} \qquad\qquad \boxed{R = \frac{V}{V^*}}$$

bulk density

retardation factor   porosity   ratio between 2 velocity

V = seepage velocity actual velocity of water into the groundwater (hidraulic gradient + porosity)

V* = apparent velocity; velocity of the contaminant in an acquifer

ACQUIFER made of particles, organic particles

the cont.
2) is sorpted into MOMENT organic C (stay here)
3) then is desorped MOMENT and moves at the same velocity of groundwater
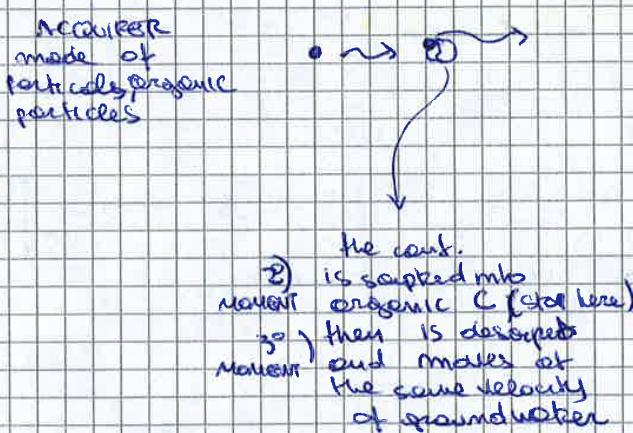
1) contaminant dissolved in groundwater (no pure phase); moves in acquifer of the same velocity of water V; but the contaminant could be sorbed by soil.

If we sum the movement of this 3 phase the velocity V* is lower the V of the groundwater.

esercizio:

$\rho_b = 2 \, g/cm^3$

$f_{oc} = 0,5$

$m = 0,24$

$K = 10^{-3} \, cm/s$

$\frac{dh}{dx} = 0,001$

contaminant data:

$\log K_{ow} = 3,36$

$MW = 128,17 \, g/mol$

$a = 0937$

$b = -0,006$

$$\log K_{oc} = a \, \log K_{ow} + b$$

$$K_{oc} = 1388 \; (\approx 1400) \; ml\,w/g_{oc}$$

$$K_d = f_{oc} \cdot K_{oc} = 0,005 \, \frac{g_{oc}}{g_{soil}} \cdot 1400 \, \frac{ml\,w}{g_{oc}} = 7 \, \frac{ml\,w}{g_{soil}}$$

$$TH_{GAC} = \frac{V_{GAC}}{TA_{GAC}} = \frac{1,44 \ m^3}{0,664 \ m^2} = 2,11 \ m$$

$$NT_S = \frac{2,11 \ m}{0,91 \ m} = 2,32 \rightarrow 3$$

↓

3 tanks
in depth

→ we
need ⑫

$$NT \cdot V = 12 \cdot 0,151 \ m^3 = 1,815 \ m^3 \qquad \rightarrow \text{total volume in the barrier}$$

$$M_{GAC} = 480 \ kg/m^3 \cdot 1,815 \ m^3 = 871 \ kg \qquad \cdot 0,01 \ \frac{kg}{kg} \ S_{GAC}$$

di quantità   ↓
adsorbita   8,71 kg   ✗

$$M_t = Q \cdot (C_{in} - C_{fin}) = 20 \cdot 10^{-3} \ \frac{m^3}{s} \cdot \left(5000 \ \frac{mg}{m^3} - 100 \ \frac{mg}{m^3}\right)$$

amount of cont.
we have to
remove

$$= 9,8 \ \frac{mg}{s} \cong 0,85 \ kg/d$$

exhaustion
time
$$T = \frac{S}{M_t} = \frac{8,71 \ kg}{0,85 \ kg/d} \cong 10 \ d$$

55.4)

$P_1 = 0,91 \ m$

$P_2 = 0,61 \ m$

$P_3 = 0,85 \ m$

$P_4 = 0,72 \ m$

12,19 m

15,24
m

P1   P2

P4   P3

$m = 0,35$

$\rho_c = 0,8 \ g/cm^3$

thick
of free
product
above the
water

surface

free
product

water
table
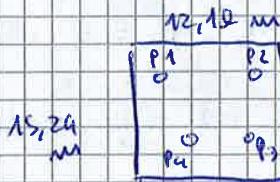
$A = 185,77 \ m^2$
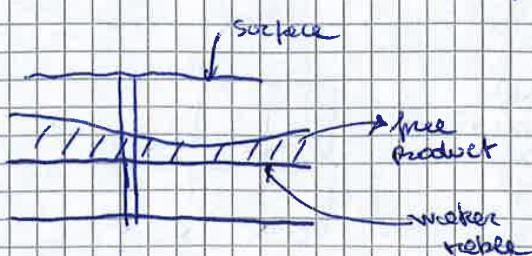
$$A = 15,24 \ m \cdot 12,19 \ m = 185,8 \ m^2$$

Average thickness of the free product $D = 0,72 \ m$

$$V = A \cdot D \cdot u = 51,4 \ m^3$$

$$M = \rho \cdot \cancel{m} \cdot V \simeq 41\,000 \ kg$$

11/11/2014

Esercitazione 6

$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{=}$$

ES. 1)

KNOWN → eq. constant

$$\frac{[Ca^{2+}][CO_3^{=}]}{[CaCO_3]} = 10^{-8,3}$$

quoziente di reazione
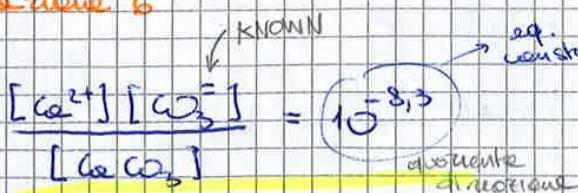
equil. between solid phase and ions in the solutions
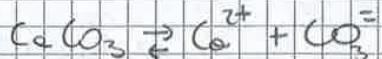
$$[Ca^{2+}] = 10^{-8,3} \cdot \frac{[CaCO_3]}{[CO_3^{=}]} = 10^{-8,3} \cdot \frac{\boxed{1}}{\boxed{10^{-5}}} = 10^{-3,3} \ \frac{mol}{\ell}$$

because is solid

dato

ES. 2)   ELECTRO NEUTRALITY

$$2[Ca^{2+}] + [H^+] = 2[SO_4^{=}] + [OH^-] + [Cl^-]$$

balance betw. positive charges and negative charges

2 positive charges   2 negative charges

$$2[Ca^{++}] = -10^{-4} + 2(6 \cdot 10^{-3}) + 10^{-10} + (3 \cdot 10^{-4}) = 6,1 \cdot 10^{-3} \ \frac{mol}{\ell}$$

We calculate this from pH = 4   dato   conc. of OH⁻   dato

$$\frac{[CaSO_4]}{[Ca^{2+}][SO_4^{=}]} = \frac{1}{(6,1 \cdot 10^{-3})(6 \cdot 10^{-3})} = 10^{4,4}$$

$$K = 10^{4,62}$$

the product is higher; 1 part may react and form CaSO₄

se le 2 specie reagiscono tra loro il DENOM. diventa + piccolo e il n° cresce e tende verso K_eq

cfr :
the system is not in equilibrium, the value we obtain is different

$$10^{4,4} < K$$

denominatore + grande

ZERO ORDER

Rate law $v = K$
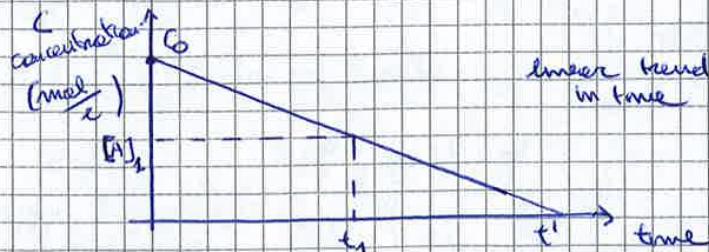
$$[A]_t = [A]_0 - Kt$$
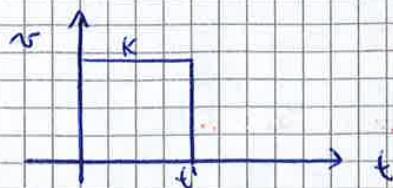
linear trend of C $\Rightarrow$ the velocity of react
in time
is constant in time
and doesn't depends
on concentration in
system

half-life
time $t_{1/2} = \dfrac{[A]_0}{2K}$

demonstration:

$$[A]_{\frac{1}{2}} = [A_0] - Kt_{\frac{1}{2}}$$

$$\frac{[A_0]}{2} - [A_0] = -K t_{1/2}$$

$$2[A_0] - [A_0] = 2K t_{\frac{1}{2}}$$

FIRST ORDER

$$\ln[A]_t = \ln[A]_0 - Kt$$

$$\frac{[A]_t}{[A]_0} = e^{-Kt}$$

Velocity at
which subst.
is consumed
in time

$v = K[A]$ $v = -\dfrac{d[A]}{dt}$

reaction rate
in time
slow down

$A_0 \rightarrow \emptyset$
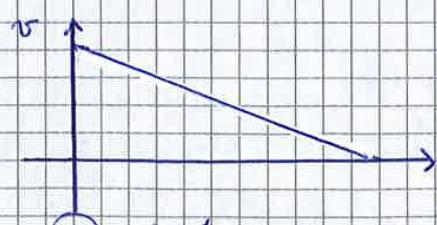
max.
amount
of subst.

$$t_{1/2} = \frac{0,693}{K} \rightarrow \ln 2$$

ES. 6)

H_2S 0,2 atm

1° parte)

$$H_2S_{(g)} \rightleftarrows \boxed{H_2S_{(aq)}}$$
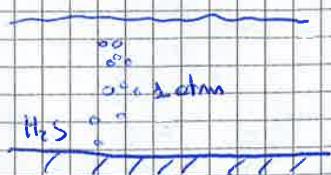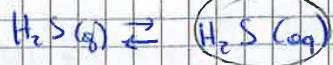
equilibrium described by $H = 10^{0,99} \frac{atm \cdot l}{84 \cdot mol}$

$$H_2S \rightleftarrows \boxed{HS^-} + H^+ \qquad K_1 = 10^{-7,02} \; mol/l$$
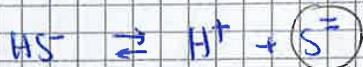
$$HS^- \rightleftarrows H^+ + \boxed{S^=} \qquad K_2 = 10^{-13,9} \; mol/l$$

PH = 6.0

$$H = \frac{P_{H_2S}}{[H_2S]_{aq}} \quad \rightarrow \quad [H_2S]_{aq} = \frac{P_{H_2S}}{H} = \frac{1 \, atm}{10^{0,99} \frac{atm \cdot l}{mol}} = 0,102 \; \frac{mol}{l}$$

$[HS^-]$

$$\frac{[H^+][HS^-]}{[H_2S]} = 10^{-7,02} \qquad [HS^-] = \frac{10^{-7,02} \cdot 0,102 \frac{mol}{l}}{10^{-6} \, mol/l} \; \rightarrow \; dal \; pH$$

$$= 9,8 \cdot 10^{-3} \; mol/l$$

$[S^=]$

$$\frac{[H^+][S^=]}{[HS^-]} = 10^{-13,9} \qquad [S^=] = \frac{10^{-13,9} \, mol/l \cdot 9,8 \cdot 10^{-3} \, mol/l}{10^{-6} \frac{mol}{l}}$$

$$= 1,2 \cdot 10^{-10} \; mol/l \quad \text{is negligible in compar. with } [HS^-]$$

2° parte)

$$CH_2Br_2 \rightarrow \text{may react with } HS^-$$

$$CH_2Br_2 + HS^- \rightarrow \text{new measr} \text{ decreas the conc. decreas from}$$
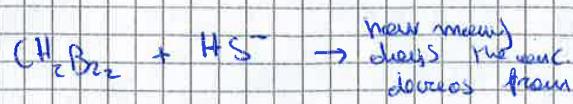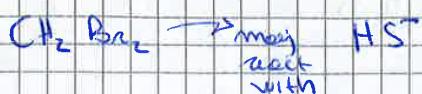
the conc. is very high and doesn't affect the equation

$$5,25 \cdot 10^{-5} \; l/mol \cdot s$$

$$\frac{d[CH_2Br_2]}{dt} = -K[CH_2Br_2][HS^-] \qquad [CH_2Br_2] \ll [HS^-]$$

pseudo first order kinetics $\rightarrow$ we can calculate k'

$$k' = k[HS^-]$$

$$\frac{1}{4} CH_2O + \frac{1}{5} NO_3^- + \frac{1}{5} H^+ \rightarrow \frac{1}{10} N_2(g) + \frac{1}{4} CO_2(g) + \frac{7}{20} H_2O$$

$$1 NO_3^- \quad : \quad \frac{5}{4} CH_2O$$
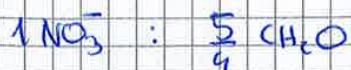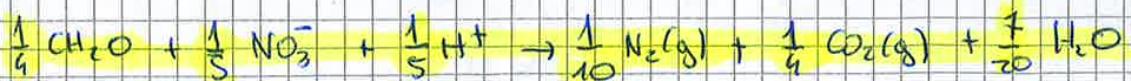
$$NO_3^- : \quad 1,2 \ mg \ NO_3^- \cdot \frac{1g}{1000mg} \cdot \frac{1 \ mol}{62 \ g} = 1,9 \cdot 10^{-5} \ mol \rightarrow \text{amount of } NO_3^- \text{ in the sistem}$$

$$\boxed{2 \cdot 10^{-5} \ \frac{mol}{CH_2O}} \cdot \frac{1 \ mol \ NO_3^-}{\frac{5}{4} mol \ CH_2O} = 1,7 \cdot 10^{-5} \ mol \ NO_3^- \rightarrow \text{amount required by reaction}$$

$$\rightarrow 1 : \frac{5}{4} = x : 2 \cdot 10^{-5}$$

numero di pmole

$1°$ part → aerobic → is consumpted

$2°$ part → anoxic → little part of remanent NO_3^-

we have a remanent little quote of NO_3^-

is enough to degradare the substance

Groundwater contaminated with PCE, old contamination

Declorurotion:

PCE C_2Cl_4 ($^{+2}$ $^{-1}$)

TCE C_2HCl_3 ($^{+1}$ $^{+1}$ $^{-1}$) → H-C = C-Cl

H C ≡ CH

DCE $C_2H_2Cl_2$ ($^{+1}$ $^{+1}$ $^{-1}$)

VC C_2H_3Cl ($^{-1}$ $^{+1}$ $^{-1}$)

$H_2C = CH_2$ ($^{-2}$ $^{+1}$ C_2H_4) → H_3C-CH_3 → CO_2, H_2O, Cl^-

→ voglio far sparire tutti gli accettori in modo di avere solo H_2 come accettore
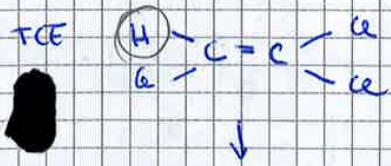
we need Hydrogen H_2 and also an anaerobic and reactive environment

all the oxidant species ← we need to consume O_2 ecc.. to reach an anaerobic environment
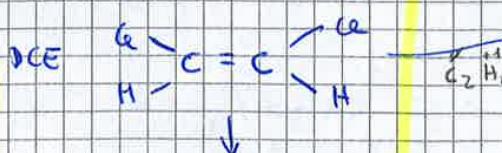
to do this we use ethanol because ethanol and all these species are involved in biological process that consume the oxidant
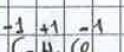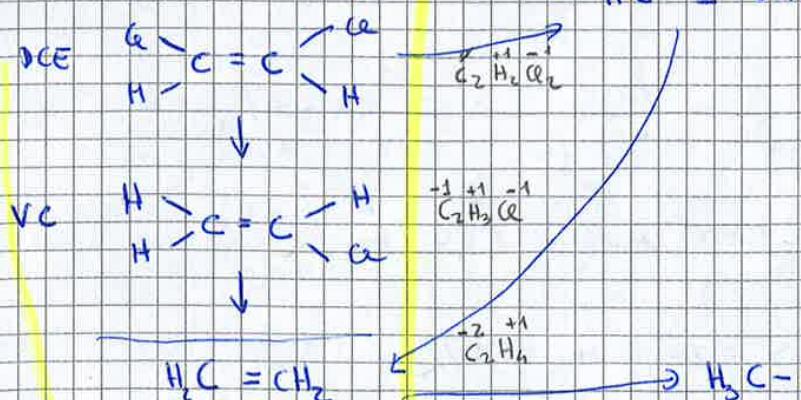
quanto etanolo dobbiamo introdurre x avere completa scomparsa di O_2 e altri accettori

$\int$ etanol m3 di acquifero

C si riduce | H si ossida

declorurazione riduttiva: è necessario idrogeno libero e che la falda si trovi in assenza di O_2 e di altri accettori di elettroni, falde in condiz. riducenti. tab. 1.1 → diversi accettori di e^- (no condiz. riducenti) → x portare a condizioni riducenti occorre far sparire accettori di e^-. Prima processi ossidi e poi anossici (si usa etanolo) → NO_3^- SO_4^{2-} $Fe(II)$ (consumo O_2)

$$6 Fe^{3+} + 0.5 \, C_2H_5OH + 1.5 \, H_2O \rightarrow 6 Fe^{2+} + 6 H^+ + CO_2$$
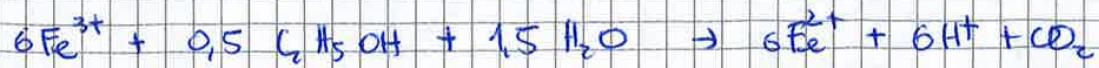
1 mol Fe   55,8 g

1 mol EtOH   46 g

$$\frac{46 g}{(12) \cdot 55,8} = \frac{46}{669,6} = 0,0687 \, g \, EtOH/_{g \, Fe^{3+}}$$

$$\frac{6}{0.5}$$

$$0,8 \, g \, Fe^{3+}/_{kg \, acq} \cdot 1740 \, \frac{kg}{m^3} = 1392 \, \frac{g \, Fe^{3+}}{m^3}$$

$$1392 \, \frac{g \, Fe^{3+}}{m^3} \cdot 0,07 \, \frac{g \, EtOH}{g \, Fe^{3+}} = 97,4 \, g/m^3$$

$$\hookrightarrow + (10,3) \, g/m^3 = 108 \, g/m^3_{acq}$$

this amount is
10 times of
the total

this suggerebbe anche consumare
metalli in forma ossidata, ma → Fe III → K red
Ferro → è legato a particelle matrice   → parte
acquifero → in realtà non   → sottostimiamo   → di tanto
sarei mai disponibile a reazioni   la quantità   perché ethel
biologiche   di etanolo   10 volte
  ↳ this suggerebbe considerare   le totale
    solo la quantità non legata   degli altri
    che si trova nell'H₂O   e di acqui

1.4   Yes because if in the site we have condition in table 1.1
    we have 3 well : all of them are in aerobic condition

→ mainly involved
in contamination

ACQUIFER

not
involved
in contam.
process

flux
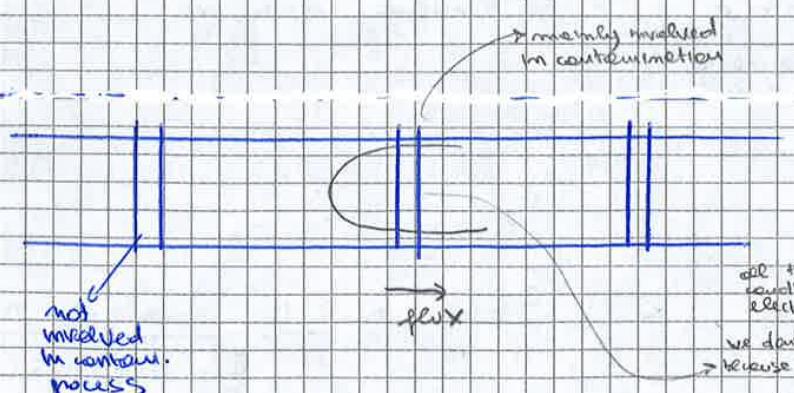
all the 3 well are in aerobic
condition and have also other
electron acceptor:

we don't see the reductive dega of PCE
→ because we have O₂, no CH₄, no metals
    generated   in reductive
    by anaerobic   states
    processes

Il processo fino a VC avviene se ambiente è riducente e anaerobico:
→ quando endo pozzo → ossigeno e altri accettori → no reductive cond.
No generation of methane → the env. is not in anaerobic conditions
  ↳ table 1.1 + ethanol
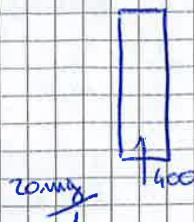
QUESTION 2)

2nd exp.

$\dfrac{M_{cr}}{M_i}$ → quantità di cromato rimosso

→ quantità di ta iniziale

20 mg/l   400

rimuoviamo una certa quantità di cromato nel sistema

porosity → / volume of column

$$PV = \boxed{\varepsilon \cdot \dfrac{\pi}{4} D^2 L} = 0.55 \cdot \dfrac{\pi}{4} \cdot (0.03)^2 \cdot 0.5$$

$$= 1.94 \cdot 10^{-4} \, m^3 \quad \to \text{volume of voids inside the column} \quad (\text{pore volume})$$

amount of Cr we removed

$$M = V \cdot C$$

$$M = 400 \; PV \cdot C = 400 \cdot 1.94 \cdot 10^{-4} \, m^3 \cdot 20 \, g/m^3 = \underline{1.55 \, g}$$

n° of pore volume after which we have the exaustion of the column

caratteristic conc. of the solution that passed through the column

absolute amount of cromate we remove from the system

$$M_{ZVI} = \rho_b \cdot V = \rho_b \cdot \dfrac{\pi}{4} D^2 L = 3000 \; \dfrac{kg}{m^3} \cdot \dfrac{\pi}{4} \cdot (0.03)^2 \cdot 0.5 \, m$$

amount of zero valent iron in the column

$$= 1.06 \, kg$$

$$CRC = \dfrac{1.55 \, g \, Cr}{1.06 \, kg \, ZVI} = 1.47 \, g \, \dfrac{Cr}{kg \, ZVI}$$

cromate reduction capacity

QUESTION 3)

hydr. cond. of aq. $8 \cdot 10^{-4} \, m/s$

hydr. cond. of barrier $4.7 \cdot 10^{-4} \, m/s$

Barrier is not suitable to treat the pollution in the aquifer. because the $k_{aq.eq.}$ is higher than $k_{barrier}$; when water meet the barrier meet a resistence e tende e possibre intorno alla barriera; non intercetta nelle maniera e adeguata il flusso di contaminante.

Dobbiamo costruire una barriera con $k = o$ maggiore della k circostante. la barriera deve rimuovere Cr e PCE e DCE. lo spessore della barriera è la somma degli spessori x rimuovere Cr PCE e DCE

TCE

$$L_{PRB2} = \frac{2h \cdot 0.0192 \, m/h}{\ell u_2} \cdot \ln\left(\frac{4000 \, mg/\ell}{10 \, mg/\ell}\right) = 0.33 \, m$$

DCE

$$L_{PRB2} = \frac{7h \cdot 0.0192 \, m/h}{\ell u_2} \cdot \ln\left(\frac{500 \, mg/\ell}{10 \, mg/\ell}\right) = 0.76 \, m$$

total thickness $\quad L = 0.24 \, m + 0.76 \, m \quad = 1 \, m$

16/12/2014

Esercitazione 10

PS 1) Toluene

$C_6H_5CH_3 \quad (C_7H_8)$

concentration in soil:
$C = 500 \, mg/kg_{soil}$

$MW = 92.1 \, g/mol$

vapour pressure $\quad VP = 22 \, mmHg$

SOIL PROPERTIES:

$\rho_b = 1.8 \, g/cm^3$

$S_w = 30\%$ water satur. degree

$M = 40\%$ porosity

$T = 20°C$

$C_{sat}(O_2)$ in water $= 9 \, mg/\ell$

↓ the amount of O_2 present in the system, is enough to complete the biological degradation of toluene? (aerobic)

we have a polluted soil that we want to remediate by BIOREMEDIATION (vadose zone)

O_2 more and water in vadose zone

pollutant → soil
O_2 in → H_2O
AIR

we refer to:

$\underline{V = 1 \, m^3 (soil)}$

1) I want to know mass of cont. in $1 \, m^3$ of soil:

mass solid $\quad M_s = \rho_b \cdot V = 1800 \, kg/m^3 \cdot 1 \, m^3 = 1800 \, kg$

mass contaminant $\quad M_c = M_s \cdot C = 1800 \, kg \cdot 500 \, mg/kg = 900 \, g$

2) Amount of O_2 for completely biodegradate this amount of toluene:

$$C_7H_8 + 9O_2 \rightarrow 7CO_2 + 4H_2O$$

1 mol toluene $\quad 92.1 \, g/mol$

9 mols O_2 $\quad 288 \, g/mol$

mass of needed oxygen

$$R = \frac{MO_2}{MT} = \frac{288 \, g/mol}{92.1 \, g/mol} = 3.13 \, \frac{g \, O_2}{g \, T}$$

oxygen demand $\quad M_c \cdot R = 900 \, g \cdot 3.13 \, g/g = 2814 \, g \quad (1 \, m^3)$

amount of oxyg. we need for biodegr. toluene

1) SORBED $\qquad$ $M_{TS} = M \cdot S = 1800 \, kg \cdot 135 \, \frac{mg}{kg} = 243,6 \, g$

$\qquad\qquad\qquad\qquad\qquad\qquad$ (dalla ρ_0) $\qquad\qquad\qquad\qquad$ mass of toluene in 1 m³ of acquifer

$1 \, m^3 \leftrightarrow 1800 \, kg$
(this amount)
$M = \rho \cdot V$

amount of solid matter in 1 m³

2) DISSOLVED

$M_{TD} = V \cdot M \cdot C_w = 1 \, m^3 \cdot 0,35 \cdot 20 \, g/m^3 = 7,0 \, g$

total mass of toluene in 1 m³ of acquifer

$M_c (1 m^3) = 243,6 \, g + 7,0 \, g = 250,6 \, g$

$\hookrightarrow$ è la parte da rimuovere con un biological process

$R = 3,13 \quad g O_2 / gT \rightarrow$ è lo stesso calcolato prima

OD (oxygen demand) $= 250,6 \, g \cdot 3,13 \, g \, O_2 / gT = 787,6 \, g$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (1m³)

$M_{O_2} = V \cdot M \cdot C_{O_2} = 1 m^3 \cdot 0,35 \cdot 4 \frac{g}{m^3} = 1,4 \, g \ll 784 \, g$

amount available for biodegradation process

ES.3) PROFILE (ex-situ)

soil contamination by hydrocarbon (HC)

kg soil contaminated soil $\rightarrow 3 \cdot 10^5 \, kg$

Contamination is due to: light HC (c<12) $\Rightarrow C_6 H_{14}$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ hydrocarbon $\qquad$ exane

meno di 12 atomi di C

conc. of Hydro. in soil $\quad 30 \, g/kg$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ natural present

In soil we have also $\begin{cases} N \\ P \end{cases}$
$\qquad\qquad\qquad\qquad N \qquad 0,22 \, g/kg$
$\qquad\qquad\qquad\qquad P \qquad 0,27 \, g/kg$

$\boxed{640 \, kg \, N \\ 85 \, kg \, P} \rightarrow$ da aggiungere x il processo di degradazione

Composition of bacteria : $C_5 H_7 O_2 N$

to calculate optimum ratio between C:N:P $\rightarrow$ a lot of consideration

to calculate C:N we must consider how much C and N are present in bacteria molecule

So the amount of N and P required is:

N: $\quad 120 : 7522 = 14 : X \qquad\qquad X_N = 8,77,56 \ kg \quad > 706 \ kg$

P: $\quad 120 : 7522 = 3,1 : X \qquad\qquad X_P = 194,32 \ kg \quad > 136 \ Kg$

the amount of N
and P is not
enoug to
complete biodeg.

in cui deve rimanere il contaminante nella barriera

tempo per consumo completo

$$t = \frac{L_{PRB}}{v^*} \qquad L_{PRB} = t \cdot v^* = \frac{1}{k'} \ln \frac{c_0}{c} \cdot v^*$$

→ we have to use v not v^*

costante cinetica

cinetica 1° ordine
$$\ln c = \ln c_0 - kt$$

$$\ln \frac{c_0}{c} = k't \qquad \to \qquad t = \frac{1}{k'} \cdot \ln \frac{c_0}{c}$$

$$\left[t_{1/2} = \frac{\ln 2}{k'} \qquad \to \qquad k' = \frac{\ln 2}{t_{1/2}} \right]$$

$$L_{PRB} = \frac{v^* \cdot t_{1/2}}{\ln 2} \cdot \ln\left(\frac{c_0}{c}\right) \qquad C_{fmole} = MCL_{co}$$

$$= \frac{\overset{1,4 \cdot 10^{-5}}{1,8 \cdot 10^{-6} \frac{m}{s}} \cdot 1h \cdot \frac{3600s}{1h}}{\ln 2} \cdot \ln\left(\frac{15 \frac{mg}{\ell} \cdot \frac{10^3 \mu g}{1 mg}}{10 \frac{\mu g}{\ell}}\right)$$

$$= 0,0683 \, m$$

Se usassi v al posto di v^* $\quad L_{PRB} = 0,532$

2) $\quad V_{SW} = 500 \, m^3 \qquad\qquad M_{sample STW} = 1100 \, t \qquad\quad \theta_v = 18\% = 0,18 \cdot \frac{V_W}{V_{t_{s(DRY)}}}$

$\rho_{grain} = 2,65 \, kg/dm^3 \quad \frac{10^3 m^3}{dm^3}$

correction:
M_W = mass of water
M_S = mass of dry soil

M_{WS} = $M_W + M_S$ = mass of the wet soil

$$M_{sample STW} = 1100 \cdot 10^3 kg$$

A) $\quad \rho_b = \rho_{H_2O} \cdot \theta + \rho_g (1-m) + \left(1 - \frac{\theta}{m}\right) m \rho_{air}$

$$\frac{M}{V} = 2'200 \, \frac{kg}{m^3}$$

$$m = \frac{-\rho_b + \rho_{H_2O} \cdot \theta + \rho_g - \theta \rho_{air}}{(\rho_g - \rho_{air})} = \frac{-2200 \frac{kg}{m^3} + 1000 \frac{kg}{m^3} \cdot 0,18 + 2650 \frac{kg}{m^3} - 0,18 \cdot 1,225}{(2650 - 1000 \frac{kg}{m^3})}$$

$$= 0,38$$

$\left[\frac{M_W}{M_S} = 0,18\right.$

$m = 0,3$

$\frac{V_s}{V} = 1 - m$

$V_s = \frac{M_s}{\rho_{grain}} = \frac{932 \, t}{2,65 \, \frac{t}{m^3}} = 350 \, \frac{t}{m^3}$

$\frac{M_{WS} - M_S}{M_S} = \frac{M_{WS}}{M_S} - 1 = 0,18$

$\frac{M_{WS}}{M_S} = 1,18$

$\left. M_S = 932 \, t \right]$

$M_S = M_{WS}/1,18 = 1100/1,18$

0.3)

$15 mm = 0,5 cm$

$C_8 H_{10}$

$M_w = 106 \frac{g}{mol}$

$h = 5 mm$

$k_a = 0,3 + 0,2 \cdot u_{10}$ (cm/s)
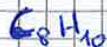
$P_v = 45 \, mmHg$

$S = 0,171 \, g/l$

$\rho = 0,88 \, g/cm^3$

$T = 25°C = 298 \, K$

$u_{10} = 3 \, m/s$

$H = \frac{P_v}{S} = \frac{45/760 \, mmHg \cdot \frac{mmHg}{1 \, atm}}{0,00161 \frac{mol}{l}} = 36,78 \, \frac{atm \cdot l}{mol}$

$H^* = \frac{H}{R \cdot T} = \frac{36,78}{0,082 \cdot 298} = 1,505$

$\quad 0,171 \, g/l \, / \, 106 \frac{g}{mol} = 0,00161 \, \frac{mol}{l}$

$k_a = 0,3 + 0,2 \cdot 3 \, m/s = 0,9 \, \frac{cm}{s}$

anche con $S \cdot H^*$

$C_g = \frac{P \cdot M_w}{RT} = \frac{45/760 \, atm \cdot 106 \frac{g}{mol}}{0,082 \cdot 298 \, K \, \frac{l \cdot atm}{mol \cdot K}} = 0,257 \frac{g}{l} = 0,257 \, \frac{mg}{cm^3}$

da

$PV = nRT \rightarrow PV = \frac{M}{MW} RT$

$\left(\frac{M}{V}\right) = \frac{P \, M_w}{RT}$

$\rightarrow C_8$

$\phi = k_a \cdot (C_g - C_a) = 0,231 \, \frac{mg}{s \cdot cm^2}$

flusso che va in atmosfera

$\quad \frac{cm}{s} \quad \frac{mg}{cm^3}$ =0

oppure: $\rho = 0,88 \, g/cm^3$

$\frac{0,88 \cdot 0,5 \, cm}{cm^3} \rightarrow M(1 \, cm^2) = 0,44 \, g/cm^2$

$h = 5 \, mm$

$0,5 \, cm$

$1 \, cm^2$

$440 \, mg/cm^2$

$0,231 \, \frac{mg}{s \cdot cm^2} \, / 0,5 \, cm = 0,462 \, \frac{mg}{cm^3 \cdot s}$

$\frac{440}{0,230} = 31,8 \, mm$

$t = \frac{880 \, \frac{mg}{cm^3}}{0,462 \, \frac{mg}{cm^3 \cdot s}} = 1'904,76 \, s \rightarrow 31 \, minuti$

dopo 15 minuti il 1% circa del contaminante non evaporato

$$S_A = H^* \cdot S_{H_2O} = 3{,}07 \cdot 10^{-2} \cdot 31{,}5 \; \frac{mg}{l} = 0{,}967 \cdot \frac{mg}{l} = 3{,}67 \cdot 10 \; \frac{mg}{l}$$

$$C_{TOT} = S_A \cdot n \cdot (1 - S_W) + S_{H_2O} \cdot n \cdot S_W + S_{ads} \cdot \rho_b$$

$$= 3{,}67 \cdot 10^{-3} \frac{mg}{l} \cdot 0{,}2 \cdot (1 - 0{,}40) + 31{,}5 \frac{mg}{l} \cdot 0{,}2 \cdot 0{,}40 + 1 \cdot 178{,}41 \cdot \frac{2650 \cdot 10^{-3}}{...}$$

$$= 3'125{,}30 \; \frac{mg}{l}$$

$$M_{TOT} = \frac{C_{TOT}}{\rho} = \frac{3'125{,}30 \; \frac{mg}{l}}{2650 \; \frac{g}{l} \cdot \frac{10^{-3} \, kg}{1 \, g}} = 1'179{,}35 \; \frac{mg}{kg}$$

$$1'474{,}19 \; \frac{mg}{kg}$$

$$i'120 \; \frac{g}{l}$$

ES. dispense retard. factor R

$$\rho_b = 2 \, g/cm^3 \qquad\qquad m = 0,24$$

$$0,005 = f_{oc} \qquad\qquad\qquad k = 10^{-3} \, cm/s \qquad v \, ?$$

$$\qquad\qquad\qquad\qquad\qquad i = 0,001$$

$$C_{10}H_8 \qquad R \, ?$$

$$log \, k_{ow} = 3,36 \qquad k_{ow} = 2290$$

$$MW = 128,7 \, g/mol$$

$$a = 0,937 \qquad b = -0,006$$

$$R = 1 + \frac{\rho_b \cdot \boxed{k_d}}{m} \qquad\qquad k_d = f_{oc} \cdot k_{oc}$$

$$\qquad\qquad\qquad\qquad\qquad log \, k_{oc} = a \, log \, k_{ow} + b$$

$$\qquad\qquad\qquad\qquad\qquad\qquad = 3,14$$

$$k_d = f_{oc} \cdot k_{oc} = 6,9 \, \frac{1}{kg} \qquad\qquad k_{oc} = 1'380$$

$$2 \frac{g}{cm^3} \quad \frac{\frac{10^{-3} kg}{g}}{\frac{10^{-3} dm^3}{cm^3}} \quad = \quad 2 \cdot 10^0 \, \frac{kg}{dm^3}$$

$$R = 1 + \frac{2 \cdot 10^0 \, \frac{kg}{dm^3} \cdot 6,9 \, \frac{l}{kg}}{0,24} = 58,5$$

$$q = k \cdot i = 10^{-3} \cdot 0,001 = 10^{-6} \, \frac{cm}{s}$$

$$v = \frac{q}{m} = \frac{1 \cdot 10^{-6}}{0,24} = 4,16 \cdot 10^{-6} \, \frac{cm}{s} \qquad\qquad v^* = \frac{v}{R} = 0,07 \cdot 10^{-6} \, \frac{cm}{s}$$

ES. 5

$\frac{mg}{Kg\ dry\ soil}$

$P = H \cdot S_w \to \frac{mg}{\ell}$

atm $\frac{atm \cdot \ell}{mol}$

$\cancel{\beta = Kd \cdot C_w}$

$C_s = Kd \cdot C_w$

$\frac{mg}{Kg\ dry\ soil}$ $\frac{1}{Kg}$ $\frac{mg}{\ell}$

$\log Kow = 3,36$

$\log Koc = a \cdot \log Kow + b$

$\qquad = 2,67 \to Koc = 467,73$

$Kd = foc \cdot Koc$

$\qquad = 0,08 \cdot 467,73$

$\qquad = 37,41$

$C_s = 37,41 \cdot 31,5 \frac{mg}{\ell} = 1178,41 \frac{mg}{Kg\ dry\ soil}$

$H^* = \frac{H}{R \cdot T} = \frac{7,34 \cdot 10^{-1}}{0,082 \cdot 291} = 3 \cdot 10^{-2}$

$C_a = H^* \cdot C_w = 3 \cdot 10^{-2} \cdot 31,5 \frac{mg}{\ell} = 0,945 \frac{mg}{\ell}$

$C_w = 31,5\ mg/\ell$

$M_{TOT} = C_w \cdot n \cdot S_w + C_a \cdot n \cdot (1 - S_w) + C_s \cdot (1-n) \rho_s$ → ρ_b

$\qquad = 31,5 \frac{mg}{\ell} \cdot 0,2 \cdot 0,4 + 0,945 \cdot 0,2 \cdot (0,6) + 1178,41 \frac{mg}{Kg\ dry\ soil} \cdot (1-0,2) \cdot 2650 \frac{g}{dm^3} \cdot \frac{10^{-3}\ Kg}{g}$

$\qquad = 2,52 + \ldots = 2498,34 \frac{mg}{\ell}$

$M_{TOT} = \frac{C}{\rho_b} = \frac{2498,34 \frac{mg}{\ell}}{(1-n) \cdot 2650 \cdot 10^{-3} \frac{Kg}{\ell}} = 1178,46 \frac{mg}{Kg\ soil\ secco}$

ρ_b

sol:

N : 132 : 28 $\frac{g}{mol}$ = x : 195, 33   sol 1 = 920,84   kg

P : 280 : 31 = x : 19,53   sol 2 = ~~170,52~~   kg
                                         239,4

$P_{atm} = 0,0289 \ atm$

$S_w = 947 \ \frac{g}{\ell}$

$1 \ atm \stackrel{\triangle}{=} 760 \ mmHg \ = \ X : 22$

$M_{w \, T_2} = 12 \cdot 7 + 8 = 92 \ \frac{g}{mol}$

$S_w = \dfrac{947 \ \frac{g}{\ell}}{92 \ \frac{g}{mol}} = 0,0051 \ \dfrac{mol}{\ell}$

$H = \dfrac{P \ atm}{S_w \ \frac{mol}{\ell}} = \dfrac{0,0289 \ atm}{0,0051 \ \frac{mol}{\ell}} = 5,67 \ \dfrac{atm \cdot \ell}{mol}$

$H^* = \dfrac{H}{R \cdot T} = \dfrac{5,67}{0,082 \cdot 295} = 0,234$

$\underline{\underline{C_a}} = H^* \cdot C_w = 0,234 \cdot 8,03 \ \frac{mg}{\ell} = 1,88 \ \frac{mg}{\ell}$

$C_S = 35 \ \frac{mg}{kgsol} \qquad C_w = 8,03 \ \frac{mg}{\ell} \qquad C_a = 1,88 \ \frac{mg}{\ell}$

$M_T \atop C_7H_8 = \underset{\frac{mg}{kg}}{C_S} \cdot \underset{\frac{g}{dm^3} \cdot 10^3 \frac{kg}{g}}{\rho_b} + \underset{\frac{mg}{\ell}}{C_w} \cdot n \cdot S_w + \underset{\frac{mg}{\ell}}{C_a} \cdot n \cdot (1 - S_w)$

$= 35 \ \frac{mg}{kg} \cdot \dfrac{1800 \, g \cdot 10^{-3} \frac{kg}{g}}{dm^3} + 8,03 \ \frac{mg}{\ell} \cdot 0,3 \cdot 92 + 1,88 \ \frac{mg}{\ell} \cdot 0,3 \, (0,8)$

$= 67,43 \ \frac{mg}{\ell} \cdot 10^3 \frac{\ell}{mg} \ \rightsquigarrow \ 67,43 \cdot 10^{-3} \ \frac{g}{\ell} \ / \ 92 \ \frac{g}{mol} = 0,73 \ \frac{mol}{\ell} \cdot 10^{-3}$

$= 0,73 \cdot 10^{-3} \ \dfrac{mol}{dm^3 \cdot \frac{dm^3}{dm^3}}$

$C_7H_8 + 9 O_2 \rightarrow 7 CO_2 + 4 H_2O$

$1 : 9 = 0,73 \cdot 10^{-3} \ \frac{mol}{m^3} : X$

$= 9,73 \ \dfrac{mol}{m^3}$

$mol \ di \ O_2 = 6,57 \ \frac{mol}{m^3} \qquad M_w \, O_2 = 16 \cdot 2 = 32 \ \frac{g}{mol}$

$\boxed{M O_2} = 6,57 \ \frac{mol}{m^3} \cdot 32 \ \frac{g}{mol} = 219,24 \ \frac{g}{m^3}$

ESERCIZI SIMULAZIONE

1) $C_{TCE} = 15 \frac{mg}{\ell}$

R ? v^* ?

$R = 1 + \frac{kd \cdot \rho_b}{m} \overbrace{(1-m) \rho_g}^{\frac{\ell}{kg}} \quad \frac{kg}{dm^3}$

$\log K_{oc} = a \cdot \log K_{ow} + b$
$\phantom{\log K_{oc}} = 1,956 \qquad K_{oc} = 90,48 \frac{\ell}{kg}$

$kd = f_{oc} \cdot K_{oc} = 0,01 \cdot 90,48 = 0,9048 \frac{\ell}{kg}$

$\rho_b = \rho_g (1-m) = 2,65 \frac{g}{cm^3} \cdot (1-0,35) = 1,7225 \frac{g}{cm^3} \cdot \frac{10^3 kg}{10^3 dm^3} = 1,7225 \frac{kg}{dm^3}$

$q = k \cdot i = 4,9 \cdot 10^{-6} \; m/s$

$R = 1 + \frac{0,9048 \cdot 1,7225}{0,35} = 5,45 \qquad v = \frac{q}{m} = 14 \cdot 10^{-6} \; m/s$

$v^* = v/R = 2,5 \cdot 10^{-6} \; m/s$

PRB + ZVI $\qquad C_{\substack{max \\ TCE}} = 10 \frac{\mu g}{\ell} \qquad t_{1/2} = \frac{1h}{3600 s} \qquad L_{PRB} ?$

$L_{PRB} = v_{PRB} \cdot t = \frac{v_{PRB} \cdot t_{1/2}}{\ln 2} \ln \frac{[A_0]}{[A_1]} = \frac{14 \cdot 10^{-6} \cdot 3600 s}{\ln 2} \ln \left(\frac{15}{10 \cdot 10^{-3}} \right)$

$= 0,53 \; m$

$\ln \frac{[A_1]}{[A_0]} = -kt$

$\ln \frac{[A_0]}{[A_1]} = kt$

$v_{PRB} = \frac{q}{m} = K_{PRB} \cdot i \overset{=K \cdot i}{} = v = 14 \cdot 10^{-6} \; m/s$

$m_{PRB} = m_{acq}$

$t = \frac{1}{K} \cdot \ln \frac{[A_0]}{[A_1]} \quad \longrightarrow \quad k = \frac{\ln 2}{t_{1/2}}$

C_7H_{16} $MW_{C_7H_{16}} = 100,20 \frac{g}{mol}$ $MW_{(NH_4)_2SO_4} = 132 \frac{g}{mol}$ $MW_{Na_3PO_4 \cdot 12H_2O} = 380$

$MW_C = 84 \frac{g}{mol}$ $MW_N = 28 \frac{g}{mol}$ $MW_P = 31$

$84\% \; C \; m \; C_7H_{16}$ $132 : 28 = 100 : x$ $380 : 31 = 100 : x$

$C : N : P = 100 : 10 : 1$ $21\% \; N \; m \; sol 1$ $8,15\% \; P \; m \; sol 2$

$M_{TOT_C} = M_{TOT_{C_7H_6}} \cdot 84\% = 2330 kg \cdot \dfrac{84}{100} = 1957,2 \; kg$

$100 : 10 = 1957,2 : x \longrightarrow M_{TOT} N = 195,72 \; kg$

$100 : 1 = 1957,2 : x \longrightarrow M_{TOT} P = 19,57 \; kg$

$21 : 100 = 195,72 : x \longrightarrow \underline{M_{TOT \, sol 1} = 932 \; kg}$

$8,15 : 100 = 19,57 : x \longrightarrow \underline{M_{TOT \, sol 2} = 240,12 \; kg}$

3)

$\overline{} \boxed{} \overline{} \quad \mathbb{I} 5mm$ $H \, ? \quad H^* \, ?$ dopo 15 mm
c'è ancora contaminante?

$P = 45 \; mmHg$ Site:
$S_W = 0,171 \; g/l$ $T = 25°C = 298 K$
$\rho = 0,88 \frac{g}{cm^3}$ $u_{10} = 3 \; m/s$

(struttura xilene) C_8H_{10} $k_a = 0,3 + 0,2 \cdot u_{10} \; (m/s)$
$\frac{cm}{s} = 0,9$

$\phi = k_a \left(C_g - \underset{=0}{\cancel{C_l}} \right)$ $C_g = H^* C_W$ $P = 0,0522 \; atm$

$\frac{mg}{cm^2 \cdot s} \quad \frac{cm}{s} \quad \frac{mg}{cm^3}$ $\begin{cases} S_W = 0,171 \; g/l \\ M_{xylene} = 12 \cdot 8 + 10 \cdot 1 = 106 \frac{g}{mol} \end{cases}$

$S_W = \dfrac{0,171 \frac{g}{l}}{106 \frac{g}{mol}} = 0,00161 \frac{mol}{l}$

$\boxed{H} = \dfrac{P}{S_W} = \dfrac{0,0522}{0,00161} = \underline{36,77} \; \dfrac{atm \cdot l}{mol}$

$H^* = \dfrac{H}{R \cdot T} = \dfrac{36,77}{0,082 \cdot 298} = \underline{1,504}$

$C_g = H^* C_W = 1,504 \cdot 0,171 \frac{g}{l} = 0,257 \frac{g}{l}$
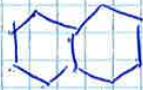
6.5) C_{max} $\dfrac{mg}{kg\,dry\,soil}$ naftalene $C_{10}H_8$ $MW = 12 \cdot 10 + 8$

$C_{10}H_8 = 128\ \dfrac{g}{mol}$

air — soil — water

$\boxed{S_{H_2O}} = 31,5\ \dfrac{mg}{\ell}$ → $31,5 \cdot 10^{-3}\ \dfrac{g}{\ell}\ /\ 128\ \dfrac{g}{mol} = 0,24 \cdot 10^{-3}\ \dfrac{mol}{\ell}$

$H = \dfrac{P\ \text{--atm}}{S\ \text{--}\frac{mol}{\ell}}$ $P = H \cdot S = 7,34 \cdot 10^{-1} \cdot 0,24 \cdot 10^{-3}$

$= 1,76 \cdot 10^{-4}\ atm$

$H^* = \dfrac{H}{R \cdot T} = 0,03076$ $C_a = H^* \cdot C_W$

$\boxed{C_a} = 0,03076 \cdot 31,5\ \dfrac{mg}{\ell} = 0,968\ \dfrac{mg}{\ell}$

$\log k_{oc} = \log K_{ow} \cdot a + b$

$= 2,67$ → $k_{oc} = 467,74$ $kd = k_{oc} \cdot f_{oc}$

$= 37,42$

$\boxed{C_{SOIL}} = kd \cdot C_W\ \dfrac{mg}{\frac{\ell}{kg}}\dfrac{mg}{dm^3} = 37,42\ \dfrac{\ell}{kg} \cdot 31,5\ \dfrac{mg}{dm^3} = 1.178,7\ \dfrac{mg}{kg}$

$\downarrow$ $\dfrac{mg}{kg\,dry\,soil}$

$C_{T_{C_{10}H_8}} = C_{SOIL} \cdot \rho_b\ +\ C_W \cdot n \cdot S\ +\ C_a \cdot n\,(1-S)$

$\dfrac{mg}{kg}$ $(1-n)\,\rho_s$ $\dfrac{mg}{\ell}$ $\dfrac{mg}{\ell}$

$\dfrac{g}{dm^3}$ $2.120\ \dfrac{g}{dm^3}$

$= 1178,7\ \dfrac{mg}{kg} \cdot (1-0,2)\ 2650\ \dfrac{g}{dm^3} \cdot 10^{-3}\ \dfrac{kg}{g} + 31,5\ \dfrac{mg}{\ell} \cdot 0,2 \cdot 0,4 + 0,968 \cdot 0,2 \cdot 0,6$

$= 2.501,48\ \dfrac{mg}{\ell}$

$\underline{C_T} = \dfrac{2.501,48\ \dfrac{mg}{\ell}}{2.120\ \dfrac{g}{\ell} \cdot 10^{-3}\ \dfrac{kg}{g}} = \underline{1,179 \cdot 10^{+3}}\ \dfrac{mg}{kg}$

$\dfrac{mg}{kg}$

ECLAMATION: FORMULE e CONVERSIONI

Gg	t(Mg)	g	mag	kg	hg	dag	g	dg	cg	mg	µg	ng	pg	MASSA
10^{12}	10^9	10^6	10^5	10^4	10^3	10^2	10	$1\,g$	$10^{-1}g$	$10^{-2}g$	$10^{-3}g$	10^{-6}	10^{-9}	10^{-12}

$10^3 Kg$

$\longleftarrow :(\cdot 10^{-n})$

$\longrightarrow \times (\cdot 10^{-n})$

es. trasformare $\left(\frac{1}{cm^3}\right) \cdot \frac{10^3 Kg/g}{10^{-6} m^3/cm^3} = 10^3 \left(\frac{kg}{m^3}\right)$

N.B. $1\,l = 1\,dm^3$
$= 10^{-3}\,m^3$

$1m^3 = 1'000\,l$

$H_2O \Rightarrow 1l = 1 Kg$

densità
$\rho = 1\,\frac{kg}{dm^3}$

$1\,atm = 760\,mm\,Hg$

N.B.
concentrazione:
$\frac{massa}{volume}$

$ppm = \frac{1\ parte}{10^6\ parti}$ es. $\frac{mg}{kg} \overset{H_2O}{=} \frac{mg}{dm^3} = \frac{mg}{l}$ $1\,ppm$

$ppb = \frac{1\ part}{10^9\ part}$ es. $\frac{\mu g}{kg} = \frac{\mu g}{dm^3} = \frac{\mu g}{l}$ $10^3\,ppb$

$ppt = \frac{1\ part}{10^{12}\ part}$ es. $\frac{ng}{kg} = \frac{ng}{dm^3} = \frac{ng}{l}$ $10^6\,ppt$

legge dei gas perfetti:

$mol = \frac{M \rightarrow massa\ [g]}{M_w \rightarrow peso\ molecolare\ \left[\frac{g}{mol}\right] \rightarrow da\ elementi\ formula\ chimica}$

$P \cdot V = m \cdot R \cdot T$ $[K]$ di solito 273K (0°C)

pressione gas [atm] di solito 1 atm   volume gas [l]   mol gas $0,082 \left[\frac{l \cdot atm}{mol \cdot K}\right]$

$M = Q \cdot C$ $\frac{m^3}{d}$ $\frac{kg}{m^3}$

$M = \rho \cdot V$ $M = C \cdot V$ [kg] $\frac{kg}{m^3}$ $[m^3]$

$mol = C \cdot V$ $\left[\frac{mol}{l}\right]$ $[l]$

$H = \frac{P_v}{S}$ $\left[\frac{atm \cdot l}{mol}\right]$ press. di vapore [atm]

$H^* = \frac{H}{R \cdot T}$ $[-]$ $0,082 \left[\frac{l \cdot atm}{mol \cdot K}\right]$ $[K]$

liquid/air (HENRY)   solubilità $\left[\frac{mol}{l}\right]$

molar fraction $X_i = \frac{m_i}{m_{TOT}}$ $x_1 + x_2 + x_3 + \ldots = 1$

$C_a = H^* \, C_w$ $C_i\ mar\ \left[\frac{mol}{l}\right]$ $\left[\frac{mol}{l}\right]$ $C_i\ in\ H_2O$

pressione parziale (DALTON) $P_i = y_i \cdot P_{TOT}$ $P_1 + P_2 + P_3 + \ldots = P_{TOT}$

frazione molare i nel gas

liquid vapor equil. (RAOULT) $P_i = P_{v_i} \cdot X_i$

pressione di vapore di i in un sistema complesso (+ contaminanti) partial pressure

pressione di vapore di i come unico contaminante

frazioni molare i nel liquido

N.B. P_v VAPOR PRESSURE = concentration of contaminant in the air (soil voids) in equilibrium with the pure phase   [CONTAM.] AIR

$\rho_z(T)$

S WATER SOLUBILITY = concentration of contaminant in the water (soil voids) in equilibrium with the pure phase   [CONTAM.] H_2O

①

CHEMICAL EQUILIBRIUM

$$a A + b B \rightleftharpoons c C + d D$$

$$K = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}$$

conc. molari $\frac{mol}{\ell}$

nell'espressione compaiono solo cost. gassose!

(liquidi e solidi puri no)
$[-] = 1$

N.B. PH

$$\begin{bmatrix} K_w = [H^+][OH^-] = 10^{-14} \\ [H^+] = [OH^-] = 10^{-7} \end{bmatrix}$$

H_2O a $25°$

pH + pOH = 14

pH = pOH = 7
neutrality

$$pH = -\log[H^+] \qquad [H^+] = 10^{-pH}$$

$$pOH = -\log[OH^-] \qquad [OH^-] = 10^{-pOH}$$

ELECTRONEUTRALITY

equilibrio tra concentrazione di anioni e cationi

$$\sum n[X^{+}] = \sum n[X^{n-}]$$

es.

$$2[Ca^{2+}] + [H^+] = 2[SO_4^{2-}] + [OH^-] + [Cl^-]$$

n° cariche
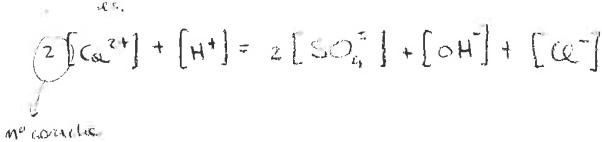
CINETICHE

generica reazione: $a A + b B \rightarrow c C + d D$

velocità di reazione = velocità variazione di concentrazione
$$r = \frac{d[C]}{dt}$$

legge cinetica: $r = K[A]^m[B]^n$

costante velocità [tempo^{-1}] di reazione

→ non necessariamente = a a e b

RO = m + n
$RO_A = m$
$RO_B = n$

ordine zero

$$r_A = K$$

$$r_A = \frac{d[A]}{dt} = -K$$

la velocità è indipendente dalla concentraz. dei reagenti

$$d[A] = -K dt$$

$$\int_{[A]_0}^{[A]_t} d[A] = -K \int_0^t dt \qquad \rightarrow [A]_t = [A]_0 - Kt$$
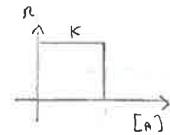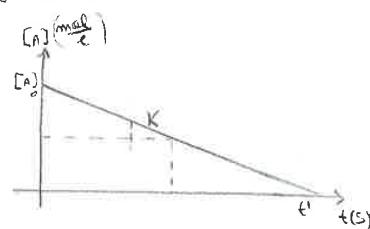
half-life time

N.B. $[A]_{t_{1/2}} = [A]_0 - Kt_{1/2}$

$\frac{[A]_0}{2} - [A]_0 = -K t_{1/2}$

$-\frac{1}{2}[A]_0 = -K t_{1/2}$

$[A]_0 = 2K t_{1/2}$

$$t_{1/2} = \frac{[A]_0}{2K}$$
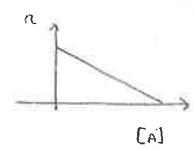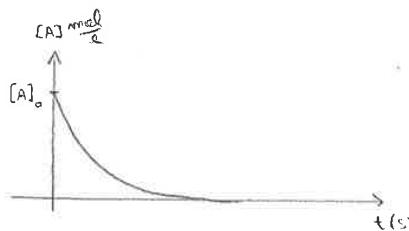
primo ordine

$$r_A = K[A]$$

$$r_A = \frac{d[A]}{dt} = -K[A]$$

la velocità è direttamente proporzionale alla concentraz. di un reagente

$$\frac{d[A]}{[A]} = -K dt$$

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = -K \int_0^t dt$$
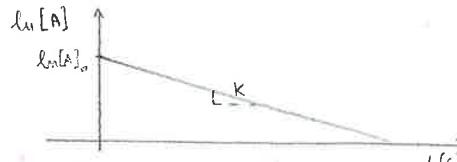
$$\ln[A]_t - \ln[A]_0 = -Kt \quad \rightarrow \quad \ln[A]_t = \ln[A]_0 - Kt$$

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -Kt \quad \rightarrow \quad [A]_t = [A]_0 \cdot e^{-Kt}$$

half-life time

$\ln[A]_{t_{1/2}} = \ln[A]_0 - K t_{1/2}$

$-\ln\frac{1}{2}[A]_0 + \ln[A_0] = +K t_{1/2}$

$\ln\left(\frac{[A]_0}{\frac{1}{2}[A]_0}\right) = K t_{1/2}$

$t_{1/2} = \frac{1}{K} \cdot \ln 2$

$$t_{1/2} = \frac{0,693}{K}$$

③

LEGGE DI DARCY

$$Q = A \cdot k \cdot \frac{\Delta h}{L}$$

$\frac{m^3}{s}$ m^2 $\frac{m}{s}$
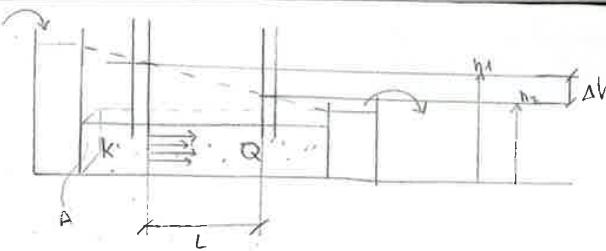
N.B. PRB

barriera efficace $K_{barriera} \geq K_{req.}$

→ altrimenti H_2O passa internno

dimens. = trovare spessore barriera - L_{PRB}

Se conosco tempi di dimezzamento sostanze
→ tempo x consumo completo

da cinetica 1° ord. $\ln \frac{C_0}{C} = K \cdot t$

$$t = \frac{L_{PRB}}{v_{PRB}} \rightarrow L_{PRB} = (t) \cdot v_{PB} = \frac{1}{K} \cdot \ln \frac{C_0}{C} \cdot v_{PRB} = \frac{t_{1/2} \cdot v_P}{\ln 2} \cdot \ln \left(\frac{C_0}{C} \right)$$

$t_{1/2} = \frac{\ln 2}{K}$

Se conosco massa di ZVI
$$L_{PRB} = \frac{M_{ZVI}}{H \cdot \rho_b}$$
altezza barriera   densità mercato

$v_{PRB} = v_{acquifero}$ se non va altro nel resto!

$$v_{PRB} = \frac{K_{PRB} \cdot i}{m}$$

Calcolare il quantitativo di X1 per biodegradare X2

1) formula chimica $n X_2 + m X_1 \rightarrow \dots$

2) pesi molecolari $MW1$ $MW2$

3) rapporto $R = \frac{m \cdot MW1}{n \cdot MW2}$

4) $X_{1 \, amount} = M_C \cdot R \; [g]$ oppure $X_{1 \, amount} = [X_2] \cdot R \; \left[\frac{mg}{l} \right] \dots$

massa contaminante g $\frac{mg}{l}$

Calcolare optimum RATIO di C:N:P in bioremediation

$$\underbrace{C : N : P}$$

the optimum ratio is the ratio we have in the cells of bacteria   dato del problema es. $P = 10\% N$

es $C_5 H_7 O_2 N$

form. da batt. $P = 10\% N$
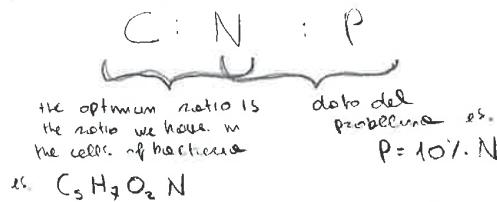
esempio $C:N:P = 5 : 1 : 0,1$ → moli
$= (5 \cdot 12) : 2 : (1 \cdot 14) : (0,1 \cdot 31)$
masse

Neumentare di N e P poste x biodegradare un HC?

1) Calcolo quantità di C in HC da biodegradare

es: $(M_{HC_0} - M_{HC_f}) \cdot \frac{gC}{mol HC} = gC$

gHC $\frac{gHC}{mol HC}$

2) dell'optimum ratio calcolo N e P e poi cfr con quello che ho

---

fabbisogno di sali con N, P...

es. $(NH_4)_2 HPO_4$ (DAP)
$NH_2 CONH_2$ (UREA)
$(NH_4)_2 SO_4$
$Na_3 PO_4 \cdot 12 H_2 O$
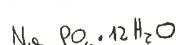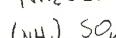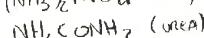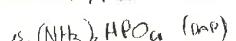
dato rapporto ottimale es. $C:N:P = 100 : 15 : 1$
in PESO o in MOLI

1) Calcolo % N e P nei sali conoscendo i MW
es. $MW_P = 31 \frac{g}{mol}$ $MW_{DAP} = 130 \frac{g}{mol}$
$130 : 31 = 100 : x$ $x = 24$

2) conoscendo C ricavo N' e P' necessari (kg)

3) Per trovare 1 kg di sale divido 1 kg di N'e P' per le % degli elementi es. DAP = P'/0,24 → $100 : 24 = P' : x$

1) conoscendo C ricavo N' e P' necessari (moli)
calcolo le moli TOT del composto e poi moltiplico per le moli C
es. $C_7 H_{16}$ M = 158 kg
$153 \cdot 10^3 / 100 \frac{g}{mol} = 1580$ mol
$mol C = 1580 \cdot 7 = 11'060$ mol

2) Per trovare i kg di sale moltiplico le moli di N'e P' per i MW dei sali

⑤