Seoul National University

457.210A.002

Environmental Engineering

MIDTERM EXAMINATION

TIME ALLOWED: 75 MINUTES

October 27, 2014

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1. Students may use two double-sided, A4 notes prepared in their own handwriting. Mechanical or electronic reproduction of any notes are not allowed.
   (앞뒷면 모두를 사용하여 A4 용지 두 장에 필요한 내용을 적어 시험에 사용할 수 있습니다. 다만, 컴퓨터로 출력하거나 복사한 것은 불가합니다.)
2. Students should bring their own calculator which is not pre-programmed with formulae from the class.
   (계산기를 사용하되, 수업과 관련된 공식이 프로그램되어 있으면 안됩니다.)
3. Be aware that the cheated student will get 80% of the lowest score in class! There is no tolerance at all.
   (주지한 바와 같이, 부정행위를 할 경우 학급 최저점수의 80%를 부여합니다. 부정행위는 절대 용납하지 않습니다.)
4. Make sure your answers includes units if appropriate. Watch your units! Prepare your answers in a logical, easy-to-follow format.
   (해당사항이 있을 경우, 꼭 단위를 기입하고, 정확한 단위를 사용하십시오. 답은 논리적이고 이해하기 쉽게 기재하십시오.)
5. This exam contains 10 questions. Each full question is worth 10 to 25 points. Total points = 165.
   (본 시험은 10 문항으로 구성되어 있으며, 각 문항의 배점은 10점에서 25점입니다. 총점은 160점입니다.)

Use following values for physical constants and properties, if needed:

Atomic weights: C, 12; Cl, 35.5; H, 1; N, 14; O, 16; P, 31; S, 32.1; Ca, 40

Density of water at 4°C: 1 g/cm^3

1. The dissociation reaction for acetic acid is as follows:

$$CH_3COOH + H_2O \rightleftarrows CH_3COO^- + H_3O^+$$

i) Indicate the conjugate acid and conjugate base for this reaction. (5 points)

Answer) conjugate acid: H_3O^+*; conjugate base:* CH_3COO^-

ii) The pK_a for acetic acid is 4.75. Calculate $[CH_3COO^-]/[CH_3COOH]$ when pH=5. Assume activity=molarity. (5 points)

Answer)

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = 10^{-4.75},\ [H^+] = 10^{-5}\ M$$

Therefore, $\dfrac{[CH_3COO^-]}{[CH_3COOH]} = 1.78$

2. Rainwater is naturally slightly acidic (pH=5.6) because of the dissolution of CO_2. Assuming that the CO_2 dissolved in rainwater is at equilibrium with atmospheric CO_2, what is the bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) concentration in rainwater? Assume activity=molarity. The partial pressure of CO_2 in the atmosphere (P_{CO2}) is $10^{-3.5}$ atm and the Henry's constant is $10^{-1.5}$ M/atm. The dissociation constants for carbonate species are given as follows:

$$H_2CO_3^* \rightleftarrows HCO_3^- + H^+, \quad K_{a1} = 10^{-6.3}$$

$$HCO_3 \rightleftarrows CO_3^{2-} + H^+, \quad K_{a2} = 10^{-10.3}$$

(15 points)

Answer)

This is an open system.

Using the Henry's law, $[H_2CO_3^*] = K_H P_{CO_2} = 10^{-1.5}\ M/atm \cdot 10^{-3.5}\ atm = 10^{-5}\ M$

$$\frac{[H^+][HCO_3^-]}{[H_2CO_3^*]} = 10^{-6.3},\ [H^+] = 10^{-5.6}\ M$$

$$\therefore [HCO_3^-] = 2.00 \times 10^{-6}\ M$$

$$\frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 10^{-10.3}$$

$$\therefore [CO_3^{2-}] = 3.98 \times 10^{-11}\ M$$

Or, if you used the equations presented in the lecture note,

$$\log[HCO_3^-] = -11.35 + pH = -11.35 + 5.6 = -5.75$$

$$[HCO_3^-] = 10^{-5.75}\ M = 1.78 \times 10^{-6}\ M$$

$$\log[CO_3^{2-}] = -21.68 + 2pH = -21.68 + 2 \cdot 5.6 = -10.48$$

$$[CO_3^{2-}] = 10^{-10.48}\ M = 3.11 \times 10^{-11}\ M$$

**The results of the two approaches are slightly different. This is because the equations presented in the lecture note are based on* $pK_{a1} = 6.35$ *and* $pK_{a2} = 10.33$. *In this question, I truncated the values of* pK_{a1} *and* pK_{a2} *to the first decimal point to make* $pK_{a1} = 6.3$ *and* $pK_{a2} = 10.3$. *This resulted in the differences in the values. Answers using either of the two approaches will get full points, if there are no calculation errors.*

3. Briefly explain the differences between DNA and RNA in the following two aspects: i) the structure and ii) the function. (10 points)

Answer)

i) the structure: the DNA has 2'-deoxyribose as sugar while the RNA has ribose; the DNA has A, T, G, C as bases while the RNA has A, U, G, C; the DNA is double stranded while the RNA is single stranded.

ii) the function: the DNA stores and transfers the genetic information while the RNA *transfers the genetic information from the DNA to ribosomes to make proteins.*

4. To study the pathogen removal kinetics, you conducted a laboratory study using a completely-mixed batch reactor (CMBR) and achieved 90% removal in 10 minutes. Assuming that the pathogen removal kinetics follows first-order reaction, answer the following:

i) Calculate the first-order reaction constant for pathogen removal by chlorine disinfection. (10 points)

Answer)

For a CMBR, following equation apply:

$$\frac{C_{final}}{C_{initial}} = e^{-kt_{final}}$$

$$k = -\frac{1}{t} ln\frac{C_{final}}{C_{initial}} = -\frac{1}{10\min} ln 0.1 = 0.230\min^{-1}$$

ii) Calculate the half-life of pathogens under chlorine disinfection. (5 points)

Answer)

The half-life of a first-order reaction, $t_{1/2}$

$$t_{1/2} = \frac{\ln 2}{k} = \frac{\ln 2}{0.230\min^{-1}} = 3.0\min$$

5. A chemical degrades in a steady-state completely-mixed flow reactor (CMFR) according to first-order reaction kinetics. The influent concentration (C_{in}) is 20 mg/L and the effluent concentration (C_{out}) is 5 mg/L. The flow rate is 500 m^3/hr and the volume of the tank is 200 m^3. Answer the following:

i) Calculate the retention time of the CMFR. (5 points)

Answer)

The retention time, t_0

$$t_0 = \frac{200\ m^3}{500\ m^3/hr} = 0.4\ hr$$

ii) Calculate the first-order reaction constant. (10 points)

Answer)

For a steady-state CMFR, following equation apply:

$$C_{out,t} = \frac{C_{in}}{1+kt_0}$$

$$k = \frac{1}{t_0}\left(\frac{C_{in}}{C_{out,t}} - 1\right) = \frac{1}{0.40\ hr}\left(\frac{20\ mg/L}{5\ mg/L} - 1\right) = 7.5\ hr^{-1}$$

iii) You are asked to improve the effluent quality to 2 mg/L and you simply decided to make the tank larger. What should be the volume of the tank? Assume that the tank still works as a CMFR. (10 points)

Answer)

Again, using following equation:

$$C_{out,t} = \frac{C_{in}}{1+kt_0}$$

$$t_0 = \frac{1}{k}\left(\frac{C_{in}}{C_{out,t}} - 1\right) = \frac{1}{7.5\ hr^{-1}}\left(\frac{20\ mg/L}{2\ mg/L} - 1\right) = 1.2\ hr$$

The volume of the new tank, V_{new}

$$V_{new} = Q \cdot t_0 = 500\ m^3/hr \cdot 1.2\ hr = 600\ m^3$$

6. Answer following questions:

i) Briefly explain the differences among bioaccumulation, biomagnification, and bioconcentration. (5 points)

Answer)

Bioaccumulation: the uptake of chemicals by an organism from either water or food (in other words, accumulation <u>via water or food</u>)

Biomagnification: a process that results in accumulation of a chemical in an organism at higher levels than are found in its own food (in other words, accumulation <u>only via food</u>)

Bioconcentration: the uptake of chemicals from the dissolved phase (in other words, accumulation <u>only via water</u>)

ii) Indicate the changes in nitrogen oxidation state for nitrification and denitrification. Give your answer in the following format: nitrification - A to B; denitrification - C to D. (5 points)

Answer)

Nitrification is a process of nitrogen oxidation from ammonium (NH_4^+) to nitrate (NO_3^-); and denitrification is a process of nitrogen reduction from nitrate (NO_3^-) to dinitrogen gas (N_2). Therefore, the answer is as follows:

nitrification - -3 to +5; denitification - +5 to 0

iii) What are the two main elements (nutrients) that should be controlled to prevent eutrophication in lakes and coastal areas? List at least three sources of the nutrients. (Three in total, not for each) (5 points)

Answer)

Nitrogen (N) and phosphorus (P).

Sources (three of the following): Human waste, animal waste, phosphate-based detergents *(for P only), agricultural runoff, fertilizers, food-processing wastes*

7. Prof. Choi came back to Korea after living in the U.S. for exactly five years. One day, he was shocked by the news that there was carbon tetrachloride with a concentration of 0.05 mg/L in U.S. drinking water. Prof. Choi drank 2 L water everyday, and he stayed in the U.S. for 350 days per year during the five years. Assume(!!!) that his body weight is 65 kg and the averaging time (AT) is 75 years (=27375 days).

i) Assuming that drinking U.S. water during the five year stay is the only exposure route for carbon tetrachloride, calculate Prof. Choi's lifetime chronic daily intake of carbon tetrachloride. (15 points)

Answer)

The chronic daily intake, CDI,

$$CDI = C\left[\frac{(CR)(EFD)}{BW}\right]\left(\frac{1}{AT}\right)$$

The chemical concentration, $C = 0.05\ mg/L$

The contact rate, $CR = 2\ L/day$

The exposure frequency and duration, $EFD = EF \times ED = 350\ days/year \cdot 5\ years = 1750\ days$

Therefore,

$$CDI = (0.05\ mg/L)\left[\frac{2\ L/day \cdot 1750\ days}{65\ kg}\right]\left(\frac{1}{27375\ days}\right) = 9.83 \times 10^{-5}\ mg/kg-day$$

ii) The carcinogenicity slope factor for oral intake of carbon tetrachloride is 0.13 kg·day/mg. What is the cancer risk for Prof. Choi? (5 points)

Answer)

$$Cancer\ risk = CDI \times SF = 9.83 \times 10^{-5} mg/kg-day \cdot 0.13\ kg \cdot day/mg = 1.28 \times 10^{-5}$$

8. A watershed receives 120 cm of precipitation a year. The average runoff coefficient of the watershed is 0.35 and the runoff contributes 100% of the river flow that drains the watershed. Infiltration is estimated to be 7.0 × 10^{-7} cm/s and evapotransporation is estimated to be 45 cm/year. Determine the change in storage (in cm/year) in the watershed over a year. (15 points)

Answer)

Input processes: precipitation (P)

Output processes: River flow out (Q_{out}), infiltration (I), evapotranspiration (E_T)

The change in storage of the watershed, ΔS

$$\Delta S = P - Q_{out} - I - E_T$$

$$\Delta S = 120\ cm/year - 120\ cm/year \cdot 0.35 - 7.0 \times 10^{-7}\ cm/s \cdot (86400 \times 365)\ s/year - 45\ cm/year$$

$$= 10.9\ cm/year$$

9. Landfills in Korea should be equipped with a clay layer having a hydraulic conductivity of $\leq 10^{-7}$ cm/s and at least 1 m in depth. For a clay layer which just meets the criteria (in other words, hydraulic conductivity = 10^{-7} cm/s and 1 m in depth), how long (in years) will it take for the groundwater flow to pass the layer? Assume that the porosity of the clay layer is 0.4 and the difference in the piezometric head between the top and bottom of the layer is 1.0 m. (10 points)

Answer)

The Darcy velocity, v,

$$v = K\frac{\Delta h}{L} = 10^{-7}\ cm/s \cdot \frac{1\ m}{1\ m} = 10^{-7}\ cm/s$$

The seepage velocity, v',

$$v' = \frac{v}{\eta} = \frac{10^{-7}\ cm/s}{0.4} = 2.5 \times 10^{-7}\ cm/s$$

The time for the groundwater flow to pass the layer, t,

$$t = \frac{L}{v'} = \frac{1\,m}{2.5 \times 10^{-7}\,cm/s \cdot 10^{-2}\,cm/m \cdot (86400 \times 365)s/year} = 12.7\,years$$

10. You took a water sample from a river and analyzed it to obtain a BOD_5 of 8.0 mg/L and a DO of 5.0 mg/L. The BOD decay constant, k, is 0.15 day^{-1}. The BOD decay constant is assumed to be the same as the deoxygenation rate constant, k_d. The river flows at a speed of 0.5 m/s and the reaeration coefficient, k_r, is 0.25 day^{-1}. All parameters are determined at 20°C, which is the same as the temperature in the river. The saturation DO concentration at 20°C is 9.2 mg/L. With these data, answer the following:

i) Calculate the ultimate BOD in the water sample. (10 points)

Answer)

$$BOD_t = L_o\left(1 - e^{-kt}\right)$$

$$L_0 = \frac{BOD_t}{1 - e^{-kt}} = \frac{8\,mg/L}{1 - e^{-0.15 \cdot 5}} = 15.2\,mg/L$$

ii) Calculate the distance downstream of the river (from the sampling point) where the DO level will be the lowest. (10 points)

Answer)

The time to the critical point, t_c,

$$t_c = \frac{1}{k_r - k_d} ln\left[\frac{k_r}{k_d}\left(1 - D_a\frac{k_r - k_d}{k_d L_a}\right)\right]$$

The initial oxygen deficit, D_a,

$$D_a = DO_s - DO = 9.2\,mg/L - 5.0\,mg/L = 4.2\,mg/L$$

The initial ultimate BOD, L_a,

$$L_a = L_0 = 15.2\,mg/L$$

$$t_c = \frac{1}{0.25\ d^{-1} - 0.15\ d^{-1}} ln\left[\frac{0.25\ d^{-1}}{0.15\ d^{-1}}\left(1 - 4.2\ mg/L \cdot \frac{0.25\ d^{-1} - 0.15\ d^{-1}}{0.15\ d^{-1} \cdot 15.2\ mg/L}\right)\right]$$

$$= 3.07\ days$$

The distance to the critical point, L_c,

$$L_c = v_{river} \cdot t_c = (0.5\ m/s \cdot 86400\ s/days) \cdot 3.07\ days = 1.33 \times 10^5\ m = 133\ km$$

iii) Calculate DO at that point. (5 points)

Answer)

The critical deficit, D_c,

$$D_c = \frac{k_d L_a}{k_r - k_d}\left(e^{-k_d t_c} - e^{-k_r t_c}\right) + D_a\left(e^{-k_r t_c}\right)$$

$$D_c = \frac{0.15\ day^{-1} \cdot 15.2\ mg/L}{0.25\ day^{-1} - 0.15\ day^{-1}}\left(e^{-0.15 \cdot 3.07} - e^{-0.25 \cdot 3.07}\right) + 4.2\ mg/L \cdot e^{-0.25 \cdot 3.07}$$

$$= 5.8\ mg/L$$

The DO at the critical point, DO_c,

$$DO_c = DO_s - D_c = 9.2\ mg/L - 5.8\ mg/L = 3.4\ mg/L$$