Water Harmony
Erasmus+

WATER HARMONY ERASMUS+

Selected laboratory courses for graduate courses on water supply and wastewater treatment

Co-funded by the
Erasmus+ Programme
of the European Union

Lab Course

Version 2

June 2018

PREFACE

The main goal of the Water Harmony Erasmus+ project is to develop improved learning and teaching tools, methodologies and pedagogical approaches using best practices. As a result, skills will be developed on multiple use of resources and long-term planning for multiple benefits in such a way that project partners will have harmonized teaching and pedagogical approaches in water related graduate education.

Development of teaching materials like lectures, text books and e-learning is a part of the project. The development of lab courses is also an important part of this process, especially to utilise some of the instruments purchased through the project. This booklet presents selected lab courses drafted jointly by the project partners.

On behalf of the project I would like to thank all the partners for their excellent contributions for this booklet.

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Water Harmony Erasmus+

Water harmony ERASMUS+ Laboratory Course

- Good Lab Practices
  - Pipettes, spectrophotometers, calibration procedures etc. – **UWM, NMBU**
- pH, Cond, Alc, Acid, Hardness, Turb, SUVA – **KPI, QTU**
- Analytical procedures
  - SS/VSS, COD, BOD – **KPI, OWL-UAS**
- Unit processes
  - Coagulation – **SJU, KPI**
  - Filtration – **SJU, OWL-UAS**
  - Adsorption - **UoJ**
  - UF & RO/NF - **CSTU**
- Operation
  - Microscopy of activated sludge – **OWL-UAS, SJU**
  - Optimizing recovery of RO under different salinity (constant pressure, recycle) – **NMBU, UoJ, UoP**
  - Impact of pH, zeta-potential, phosphates, etc on coagulation – **NMBU, KPI**
  - Ion exchange softening with co-current vs. counter-current regeneration – **KPI, NMBU**
  - Evaluation of the carbonic-acid-equilibrium – **USUCT, OWL-UAS**

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1 Good Lab Practices

1.1 Quantitative analysis. Spectrophotometric determination of Fe ions in ground water.

Lab purposes

1. Introduction to spectrophotometric analysis.
2. Preparation of the calibration graph.
3. Learning how to use micropipettes and macropipettes.
4. Learning how to take ground water samples and their preparation.
5. Familiarization with the Fe determination in natural water samples.

Theory

Introduction

Iron (Fe) is the first element in Group VIII of the periodic table. It has an atomic number of 26, an atomic weight of 55.85 and common valences of 2 and 3.

The average abundance of Fe in the earth's crust is 6.22 %. In the soil, Fe ranges from 0.5 to 4.3 %. In streams, it averages about 0.7 mg/L, and in ground water, it is 0.1 to 10 mg/L.

Iron is present in the following minerals: hematite (Fe_2O_3), magnetite (Fe_3O_4), taconite (a low-grade siliceous iron formation) and pyrite (FeS_2).

The solubility of iron compounds in water is controlled by the carbonate concentration. Because groundwater is often anoxic, any soluble iron in groundwater exists usually in the ferrous (Fe^{2+}) state, presumably as $Fe(HCO_3)_2$. On exposure to air or addition of oxidants, ferrous iron oxidize to the ferric state (Fe^{3+}) and may hydrolyze to form a red insoluble hydrated ferric oxide. Oxidation and hydrolysis of Fe^{2+} occur by the following schema:

$$4Fe^{+2} + O_2 + 2H_2O = 4Fe^{+3} + 4OH^-$$

$$4Fe^{+3} + 3H_2O = Fe(OH)_3 + 3H^+$$

Or:

$$4\ Fe(HCO_3)_2 + O_2 + 10H_2O = 4Fe(OH)_3 + 8\ H_2CO_3$$

Or

$$4\ Fe(HCO_3)_2 + O_2 + 2H_2O = 4Fe(OH)_3 + 8CO_2$$

In the absence of complex forming ions, ferric ion is not significantly soluble unless pH is very low.

Elevated iron concentration in water can cause stains in plumbing, laundry and cooking utensils.

Allowable level of iron concentration in water for irrigation is 5 mg/L and in water for drinking - 0.2 mg/L in the USA, and 0.1 mg/L in EU.

High concentration of iron in drinking water (more than 0.3 mg/L) is inadvisable since it causes turbidity of the water and results in an unpleasant taste.

Increased iron concentration causes stains on the washed underwear.

Some industries, e.g. paper, need water free of iron.

High iron concentration has a bad influence on the growth of some kinds of fish, mainly salmonids.

Principle of determination

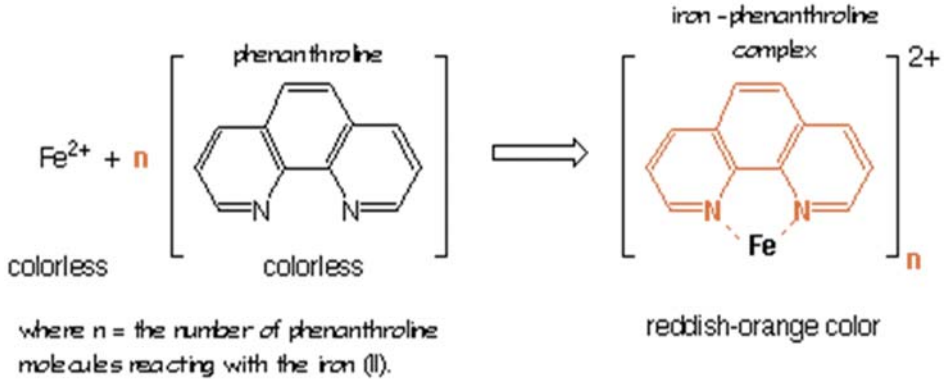
Quantitative analysis of Fe in water samples can be carried out by atomic absorption spectrophotometric method, the inductively coupled plasma method and by the method of absorption spectrophotometry.

Absorption spectrophotometry is based on a selective absorption of light radiation with specified wavelength by the solution of analyzed substance. The photo-colorimetric analysis utilizes the characteristic color of the ions. If the ions are uncolored, it is required to convert them to a colored chemical compound.

For spectrophotometric determination of iron in samples of natural, tap, or sewage water, the standard Phenanthroline Method is used. The principle of this method consists in following: The Iron brought into solution is reduced to the ferrous (Fe^{+2}) state by boiling with acid and hydroxylamine. The equation for this reaction is:

$$2NH_2OH + 4Fe^{3+} = N_2O + 4Fe^{2+} + H_2O + 4H^+.$$

After that Fe^{2+} ions treat with 1,10 phenanthroline at pH 3,2 to 3,3. The molecules of phenanthroline chelate atoms of ferrous Iron to form an orange-red complex as shown below:



In this reaction, **n** is equal to 3.

The excess of 1,10 phenanthroline in a water sample with pH range 2,9 – 3,5 insures rapid colour development. (Colour standards are stable for at least 6 months).

Interference: The interfering substances are strong oxidizing agents, cyanide, nitrite, phosphates, chromium, zinc, cobalt, copper, nickel, bismuth, cadmium, mercury, molybdate, silver.

The initial boiling of selected samples with acid and hydroxylamine (pH = 3,2 – 3,3) and following adding of excessive amounts of 1,10 phenanthroline eliminates the action of interfering substances. This is the reason why the measurements should be carried out in an excess of 1,10 phenanthroline and at recommended pH value.

Spectrophotometer

A spectrophotometer (photo-colorimeter) is an instrument designed to accurately measure the absorbance of monochromatic light by a substance placed in the beam (cell) as shown below:

Light source → Monochromatic unit → Cell → Detector → Meter

Incident Beam (I_0) → Absorbed Beam (I_t)

In the spectrophotometric study, the concentration of the iron ($Fe^{2+)}$ ions can be determined using a method with a calibration graph. In this method, a dependency between concentration and absorbance must be determined. For this purpose, colored standard solutions of known concentration of iron Fe^{2+} are prepared and their optical densities measured at the chosen wavelength. Usually, it is a linear dependence, described by a basic principle of absorption spectrophotometry - the Lambert-Beer law, described by the equation:

$$A = \log_{10} \frac{I_0}{I_t} = abc$$

where: A – absorbance,

I_0 – intensity of light incident on a sample,

I_t – intensity of transmitted light,

a – molar absorption coefficient (constant value, dependent on the light wavelength, properties of solved substance and temperature),

b – thickness of the absorbing layer,

c – concentration of the absorbing substance.

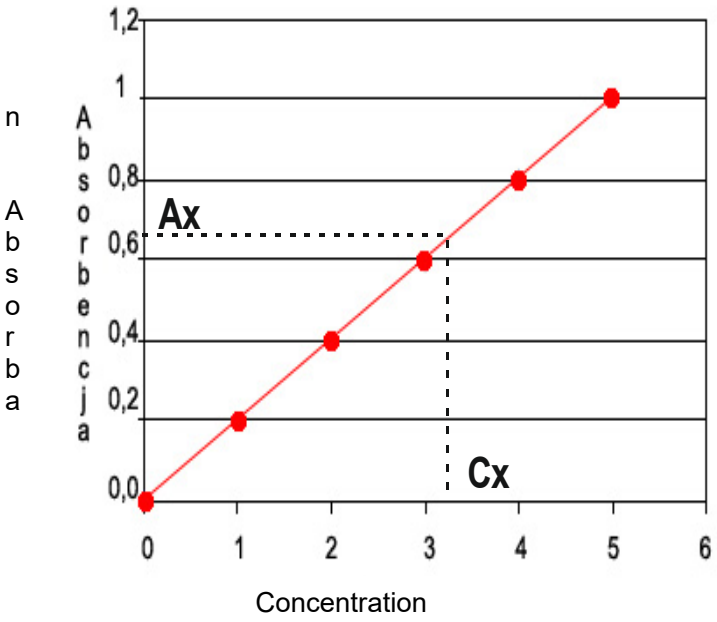
As can be seen on the equation, absorbance is proportional to the concentration of absorbing molecules and thickness of the layer.

Notice that as the concentration gets larger and larger, less and less light will pass through the solution, until the concentration gets to a point where no light will pass through and the "law" fails. It is always necessary to check whether the Lambert- Beer's law is obeyed and the plot of absorbance vs. concentration yields a straight line over the range of concentrations studied before an analysis of an unknown sample is made. Since neither cell path length **b** nor the extinction coefficient **a** are changing over the course of the experiment, we can replace them

with a constant **k**, which will be determined from the slope of linear regression data for the calibration curve.

In practice, the absorbance measurements carried out in the same cuvette or two identical cuvettes, with the same thickness ***b***.

Determination of unknown concentration in a sample (Cx) is done by reading value from the calibration graph A=f(c). A series of standard solutions with known concentrations are used for this purpose. The concentration of determined substance should be in a range of the standard solutions. The analyzed sample and the standard solution should be prepared via the same method.



Reading of concentration of analysed substance (Cx) from the calibration graph A = f(c).

Ax – absorbance of the sample.

Figure 1: Calibration graph

Equipment and reagents

- Spectrophotometer UV-Vis or photo-colorimeter for use at λ =510 nm, providing a light path of 1 cm or longer.
- Micropipettes and macropipettes,
- Nessler tubes, matched 100 mL, tall form,
- Acid-washed glassware (Washed with conc. HCl and rinse with reagent water before use to remove deposits of iron oxide),
- Separatory funnels: 125 mL,
- HCl solution (0.1 M),
- Hydroxylamine solution (Dissolve 10g NH_2OH*HCl in 100 mL water),
- Ammonium acetate buffer solution (Dissolve 250g $NH_4C_2H_3O_2$ in 150 mL water. Add 700 mL conc. acetic acid),

- Sodium acetate solution (Dissolve 200g $NaC_2H_3O_2*3H_2O$ in 800 mL water),
- Phenanthroline solution (Dissolve 100g 1.10 phenanthroline monohydrate $C_{12}H_8O_2*H_2O$ in 100mL water by stirring and heating to 80°C. Do not boil. Heating is unnecessary if two drops of conc. HCl added to the water).
- Stock iron solution (0,200 mg iron per 1mL), Weight 200.0 mg of "iron wire for standardizing" and place in a 1000 mL volumetric flask. Dissolve the handling in 20 mL 6N sulphuric acid (H_2SO_4) and dilute to mark with water. (1 mL of stock iron solution consists of 200 µg Fe).
- Standard iron solutions (10 µg/mL,). Pipet 50 mL stock solution into 1000 mL volumetric flask and dilute to the marc with water.

Safety

According to safety regulations, it is obligatory to wear a lab coat and closed shoes in the lab, safety glasses and gloves.

The wearing of safety glasses/goggles is mandatory at all time. Those students wearing prescription glasses must wear goggles over their glasses. Students without prescription lenses must wear the safety glasses provided. Contact lenses should not be worn in the lab.

Tasks performance order

1. **Preparation of reference solutions**

Prepare a series of color standards (range of Fe^{+2} concentration 0.01 -1.0 ppm) by accurately pipetting calculated volumes of standard iron solutions to measure 1 to 100 µg portions into 125-mL Erlenmeyer flasks and diluting to 50 mL by adding measured volumes of water. Add 2 mL conc. HCl and 1 mL $NH_2OH*HCl$ solution. Transfer this mixture to 100 mL volumetric flask. Add 10mL of $NH_4C_2H_3O_2$ buffer solution and 4 mL of phenanthroline solution and dilute to mark with water. Mix thoroughly and allow 10 minutes stay for color development.

Table 1: Doses of reagents to prepare 10 standard solutions (including blank solution) ranging from 1 to 100 µg Fe in final 100 mL volume (concentration of standard solutions - 0.01 – 1 mg/L of dissolved Fe)

No.	Concentration of Fe^{3+} (ppm, mg/L)	Volume of standard iron solution with concentration (10 µg Fe per 1 mL) (mL)	Volume of conc. HCl solution (mL)	Volume of the $NH_2OH*HCl$ solution (mL)	Volume of the $NH_4C_2H_3O_2$ buffer solution (mL)	Volume of the phenanthroline solution (mL)
1	0 (blank solution)	0	2,0	1,0	10	4,0
2	0.01	0.1	2,0	1,0	10	4,0
3	0.02	0.2	2.0	1.0	10	4.0
4	0.05	0.5	2,0	1,0	10	4.0
5	0.10	1.0	2,0	1,0	10	4,0
6	0.20	2.0	2,0	1,0	10	4,0
7	0.40	4.0	2,0	1,0	10	4,0
8	0.60	6.0	2,0	1,0	10	4,0
9	0.80	8.0	2,0	1,0	10	4,0
10	1.00	10.0	2,0	1,0	10	4,0

2. The samples preparation

The samples must be collected into clean glass or polyethylene bottles and slightly acidify (2 mL conc. HCl per 100mL of water sample) directly after taking.

3. Determination of total iron:

Mix the water sample thoroughly and transfer 50.0 mL of this sample into 125 mL Erlenmeyer flask. (If this sample volume contains more than 200 µg iron, use a smaller accurately measured portion and dilute to 50 mL). Add 2 mL conc. HCl and 1 mL $NH_2OH*HCl$ solution. Add a few glass beads and heat to boiling. Continue boiling until volume decreased to 15-20 mL. After cooling the product to room temperature, transfer it to 100 mL volumetric flask. Add 10 mL of $NH_4C_2H_3O_2$ buffer solution and 4 mL of phenanthroline solution. After that add distilled water up to the mark of volumetric flask. Mix thoroughly and allow of 10 minutes stay for color development. Determine the light absorbance of colored sample at λ=510 nm.

4. Determination of dissolved iron

Immediately after collection, filter the sample of water through 0,45 μm membrane filter into vacuum flask, containing 1 mL of conc. HCl per 100mL of sample. Analyze filtrate for total dissolved iron like described above. Namely, add to the filtrate1 mL NH_2OH*HCl solution. After that add a few glass beads and heat to boiling. Continue boiling until volume decreased to 15-20 mL. After cooling the product to room temperature, transfer it to 100 mL volumetric flask. Add 10 mL of $NH_4C_2H_3O_2$ buffer solution and 4 mL of phenanthroline solution. After that add distilled water up to the mark of volumetric flask. Mix thoroughly and allow of 10 minutes stay for color development. Determine the light absorbance of colored sample at λ=510 nm.

5. Determination of ferrous iron

Determine ferrous iron at sampling site because of the possibility of change in the ferrous-ferric ratio ($Fe^{+2} \leftrightarrow Fe^{+3}$) with time.

To determine ferrous iron only acidify the sample with 2 mL conc.HCl / 100mL sample at the time of collection. Fill bottle directly from sampling source and stopper. Immediately withdraw a 50 mL portion of acidified sample and add 20 mL of phenanthroline solution and 10 mL of $NH_4C_2H_3O_2$ solution with vigorous stirring. Dilute to 100 mL and measure the color intensity within 5 to 10 minutes.

Do not expose to sunlight. Color development is rapid in presence of an excess of phenanthroline. The given phenanthroline volume is suitable for less than 50μg of total iron. If larger amounts are present, use a correspondingly larger volume of phenanthroline or a more concentrated reagent.

Calculate ferric (Fe^{+3}) iron by subtracting ferrous iron concentration from the concentration of total iron.

The Use of Spectrometer

1. Turn on the instrument and allow it to warm up for about twenty minutes.
2. Rotate the wavelength selector to 510 nm. Approach the wavelength from the low end of the scale and stop at 510 nm. Do not search back and forth for the exact setting.
3. With the door of the sample holder closed, adjust the "Zero Adjust" knob to bring the needle to zero on the percent transmission scale.
4. Fill a cuvette about half or two-thirds full with the blank solution, wipe it clean, and insert into the sample holder. Close the sample door and adjust the "Light Control" knob until the meter reads 100% transmittance.
5. Replace the sample blank with your first diluted standard iron solutions and record its transmittance. Repeat with the rest of your series of diluted standard iron solutions. Recheck the zero and 100% transmittance setting, using procedures 3 and 4 above, to be certain no "drift" has occurred. If it has, redo the calibration solutions.
6. Record the spectrometer number on your report sheet, as this same spectrometer will be used for your unknown samples.

Using the spectrophotometer (photo-colorimeter), carefully measure the percent transmittance of 10 standard solutions and water probes. Record your results in the following table.

Table 2. Solutions transmittance percentage and absorbance.

Solution	% Transmittance	Absorbance (A=-logT)
0.00 mg/L Fe (blank)	100%	0
0.01 mg/L Fe		
0.02 mg/L Fe		
0.05 mg/L Fe		
0.10 mg/L Fe		
0.20 mg/L Fe		
0.40 mg/L Fe		
0.60 mg/L Fe		
0.80 mg/L Fe		
1.00 mg/L Fe		
total iron		
dissolved iron		
ferrous iron		

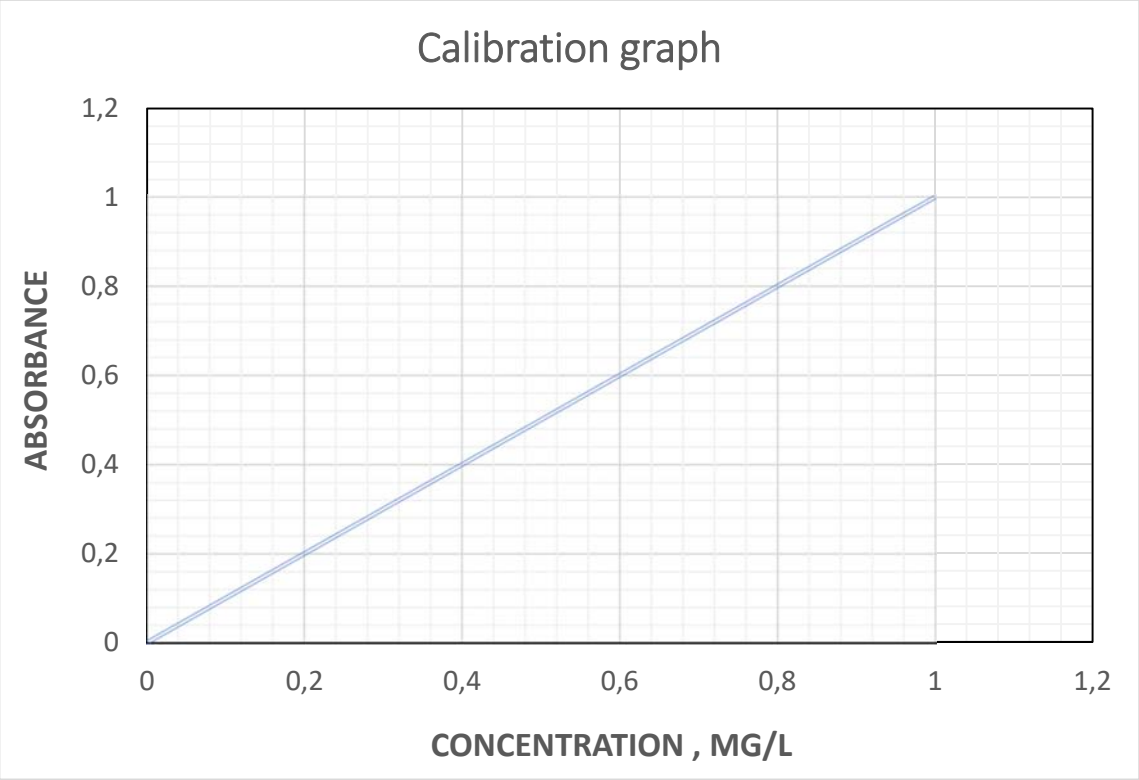
Report content

1. Describe briefly the abundance of iron distribution in Earth crust. In what state it is present in natural water and why is required to purify water from the excess of iron?

2. Describe the principle of colorimetric method used for quantitative determination of iron in water probes.

3. Describe the procedures of preparation of standard solutions and water probes for execution of colorimetric measurements. Reproduce the Table 2 in report.

Plot the calibration graph of the function: the concentration of Fe in standard solutions vs. absorbance (A) like shown below:



Draw the best fitting straight line through the points – this called the Beer-Lambert Law plot.

By using plotted line and measured data of light beam absorbance in studied samples of water, calculate the concentration of Fe in each of them. Explain the cause of the differences in results obtained.

Based on the literature, explain why the ground water samples require acidifying.

Discussion issues:

1. What is the purpose of using the hydroxylamine hydrochloride in procedures of preparation the standards and water samples?

2. The reaction: $Fe^{+2} + 2H_2O \rightarrow Fe(OH)_2 + H^+$ occurs readily. Why would this be a problem in the determination of the amount of Fe^{+2} ? What procedure was used in analytical experiments to prevent this reaction from interfering with the determination of the percent Fe^{+2} in the unknown sample?

3. Why the "blank" sample is necessary at performing of colorimetric measurements?

4. How to determine Fe^{+3} concentration in water samples using phenanthroline method?

References

1. Standard Methods for the Examination of Water and Wastewater. ISBN: 9780875532875. Author: E.W. Rice, R.B. Baird, A.D. Eaton, editors. Publisher: American Public Health Association, American Water Works Association, Water Environment Federation. Publication date: 2017. AWWA catalog no: 10086. Media Type: HARDBACK

1.2 Determination of alkalinity, acidity, hardness, pH, conductivity, turbidity and SUVA in samples of natural water.

Lab purpose

The aim of this work is to learn the standard methods of evaluation of the following water quality indicators: pH, alkalinity, acidity, conductivity, hardness, turbidity and SUVA.

Theory

The alkalinity of natural water is caused by weak acid anions and OH^- ions. Total alkalinity is characterized by concentration of ions OH^-, HCO_3^-, CO_3^{2-} and anions of other weak acids.

The acidity of natural water with pH > 4,5 is caused by free carbon (IV) oxide, humic and other weak organic acids; with pH < 4,5 by strong acids and salts of strong acids and weak bases. It has distinguished the total acidity, free acidity, free carbon (IV) oxide, aggressive carbon (IV) oxide and also acidity independent from other weak non-volatile acids.

Equipment and reagents

Equipment: pipettes (100 cm^3) – 5 ones, bulbs for the titration (250 cm^3) – 5 ones; pH-meter; Burettes.

Reactants: hydrochloric acid solutions – 0,05 M and 0,1 M; sodium hydroxide solution 0,1 M; indicators – methyl orange, phenolphthalein; EDTA standard solution, water samples.

Tasks performance order

Experiment 1**. Determination of alkalinity of the water samples.**

Alkalinity reflects the amount of substances in water that can be neutralized by strong acids. These substances are hydrocarbonates, carbonates, and hydroxides. Depending upon indicator used, one can evaluate the total alkalinity, carbonate alkalinity and alkalinity stipulated by OH^- ions.

When phenolphthalein is used as indicator, the titration of water sample with hydrochloric acid standard solution until vanishing of red color of indicator, required the consumption of hydrochloric acid standard solution V1. When methyl orange is used as indicator the titration of water sample with hydrochloric acid standard solution until its colour just changes from yellow to orange, required the consumption of hydrochloric acid standard solution V2. These data allow to calculate the alkalinity of water sample due to presence of OH^- ions (expenditure of hydrochloric acid standard solution V1), and calculate the total alkalinity (TA) of water samples with V1+V2 by equations:

$$\text{PA } (CaCO_3, \text{ mg/L}) = \frac{C \times V_1 \times 50 \times 1000}{V}$$

$$\text{TA } (CaCO_3, \text{ mg/L}) = \frac{C \times (V_1 + V_2) \times 50 \times 1000}{V}$$

Where, C is the hydrochloric acid standard solution concentration (mol/L); V is the water sample volume (mL); 50 - (1/2 $CaCO_3$) molar mass (g/mol).

To determine the composition of alkalinity:

Alkalinity consists of carbonate and hydroxide if $V_1 > V_2$; alkalinity consists of carbonate and bicarbonate if $V_1 < V_2$; alkalinity from carbon Acid salt composition; $V_1 = 0$, alkalinity only bicarbonate; $V_2 = 0$, alkalinity only hydroxide.

Step 1. Determination of phenolphthalein alkalinity of water.

Step 2. Determination of total alkalinity of water.

Experiment 2. **The determination of general acidity of water.**

Acidity refers to the total amount of material in water that can neutralize with strong bases, mainly indicating the presence of strong acids, weak acids, strong acids and weak bases, and other substances in water. There are two ways to express acidity: phenolphthalein acidity (total acidity) and methyl orange acidity.

Take a suitable amount of water (VmL) in 250 mL Erlenmeyer flask, diluted with carbon dioxide-free water to 100 mL, add two drops of methyl orange indicator, titration with sodium hydroxide standard solution until the solution color changed from orange to yellow orange, count Sodium hydroxide standard solution dosage (V1). Calculate the Methyl orange acidity (MOA) in water sample with V1.

Another sample of water (VmL) placed in 250mL Erlenmeyer flask, diluted to 100 mL with carbon dioxide-free water, add 4 drops of phenolphthalein indicator, titration with sodium hydroxide standard solution until the solution just changed to light red. Note the amount of sodium hydroxide standard solution (V2). calculate the total acidity (TA) of water samples with V2.

$$\text{MOA } (CaCO_3, \text{ mg/L}) = \frac{C \times V_1 \times 50 \times 1000}{V}$$

$$\text{TA } (CaCO_3, \text{ mg/L}) = \frac{C \times V_2 \times 50 \times 1000}{V}$$

Where, C is NaOH standard solution concentration (mol/L); V is the water sample volume (mL); 50 - (1/2 $CaCO_3$) molar mass (g/mol).

Step 1. Determination of methyl orange acidity of water.

Step 2. Determination of total acidity of water.

Experiment 3**. The determination of hardness of water.**

Total hardness of water refers to the total concentration of calcium and magnesium ions in water, including non- and carbonate hardness.

Step 1. Prepare three water samples.

Step 2. Add 5 ml ammonia - ammonium chloride buffer solution (pH = 10) and 2 or 3 drops of chrome black T indicator to the samples.

Step 3. Titrating the samples with EDTA standard solution until the color turns from wine red into pure blue.

Total permanent water hardness is calculated with the following formula:

TOTAL PERMANENT HARDNESS = CALCIUM HARDNESS + MAGNESIUM HARDNESS

The calcium and magnesium hardness are the concentration of calcium and magnesium ions expressed as equivalent of calcium carbonate. The molar mass of $CaCO_3$, Ca^{2+} and Mg^{2+} are respectively 100,1 g/mol, 40,1 g/mol and 24,3 g/mol. The ratio of the molar masses is:

$$\frac{M_{CaCO3}}{M_{Ca}} = 2{,}5 \qquad \frac{M_{CaCO3}}{M_{Mg}} = 4{,}1$$

So total permanent water hardness expressed as equivalent of CaCO3 can be calculated with the following formula:

$$[CaCO_3] = 2{,}5\,[Ca^{2+}] + 4{,}1\,[Mg^{2+}].$$

Experiment 4**. The determination of pH of water.**

In chemistry, pH (/piːˈeɪtʃ/) is a logarithmic scale used to specify the acidity or basicity of an aqueous solution. It is approximately the negative of the base 10 logarithm of the molar concentration, measured in units of moles per liter, of hydrogen ions. More precisely it is the negative of the base 10 logarithm of the activity of the hydrogen ion. Solutions with a pH less than 7 are acidic and solutions with a pH greater than 7 are basic. Pure water is neutral, at pH 7 (25 °C), being neither an acid nor a base. Contrary to popular belief, the pH value can be less than 0 or greater than 14 for very strong acids and bases respectively.

Measurements of pH are important in agronomy, medicine, chemistry, water treatment, and many other applications.

The pH scale is traceable to a set of standard solutions whose pH is established by international agreement. Primary pH standard values are determined using a concentration cell with transference, by measuring the potential difference between a hydrogen electrode and a standard electrode such as the silver chloride electrode. The pH of aqueous solutions can be measured with a glass electrode and a pH meter, or an indicator.

Equipment

- pHS-3E digital pH meter
- pH glass composite electrode
- Temperature compensation electrode
- Constant temperature water bath

Figure 1: Digital pH meter

Potentiometric determination of the solution pH: the glass electrode is the indicator electrode (-), saturated calomel electrode as the reference electrode (+) to form the galvanic cell at 25 °C, when the pH of the solution changed by 1 unit, the difference of electric potentials between indicator and reference electrodes changed by 59.0 mV. In the measurement, choosing the pH close to the water samples as the standard buffer solution to calibrate the pH meter, and keep the solution temperature constant, in order to reduce the error caused by liquid junction potential, asymmetry potential and temperature changes. Before the determination of pH of water samples, two different pH buffer solution were used to calibrate. After calibration with one pH buffer solution, the error should be within ± 0.1 pH when determining the pH of another buffer solution that differs by about 3 pH units.

The calibrated pH meter allows direct determination of the pH of the water sample or solution.

Step 1. After rinsing the electrode and the plastic cup with distilled water, rinse them with a standard buffer solution for 1 to 2 times and blot dry with filter paper.

Step 2. Perform the Calibration of the instrument with the standard buffer solution and determine the pH of the standard buffer solution.

Step 3. Determination of HCl solution pH.

Step 4. Determination of NaOH Solution pH.

Step 5. Determination of KH_2PO_4 Solution pH.

Experiment 5. **The determination of conductivity of water.**

Conductivity (or **specific conductance**) of an electrolyte solution is a measure of its ability to conduct electricity. The SI unit of conductivity is siemens per meter (S/m).

Conductivity measurements are used in routinely in many industrial and environmental applications as a fast, inexpensive and reliable way of measuring the ionic content in a solution. For example, the measurement of product conductivity is a typical way to monitor and continuously trend the performance of water purification systems.

In many cases, conductivity is linked directly to the total dissolved solids (T.D.S.). High quality deionized water has a conductivity of about 5.5 µS/m at 25 °C, typical drinking water in the range of 5–50 mS/m, while sea water about 5 S/m[2] (or 50,000 µS/cm) (i.e., sea water's conductivity is one million times higher than that of deionized water).

Equipment

- SLDS- Ⅰ digital conductivity meter
- DJS-1C type platinum black electrode
- Constant temperature water bath

Figure 2: Digital Conductivity meter

1. Conductivity G: For electrolyte solution, commonly using conductivity indicates the size of its conductive capacity. Conductance G is the inverse of resistor R, namely, G = 1/R. Conductivity unit is Siemens (S). $1S = 1\Omega^{-1}$.

It represents conductivity of the cube conductor with an electrode area of 1 m^2 and an electrode pitch of 1 m in $S \cdot m^{-1}$. For electrolyte solution, let $l/A = K_{cell}$, K_{cell} is called the cell constant. So $\kappa = Gl/A = G\,K_{cell}$

2. Molar Conductivity: $\Lambda_m = \kappa/C$ (2).

The molar conductivity Λ_m of a dilute electrolyte with strong electrolyte has the following relationship: $\Lambda_m = \Lambda^{\infty}_m - AC$ (3).

Where C is the concentration of the solution in units of mol · m^{-3}, Λ^{∞}_m is the infinite dilution molar conductivity.

Draw a straight line Λ_m to C, the intercept is $\Lambda\infty_m$.

Weak electrolyte in the infinite dilution of the solution can be fully ionized. The molar conductivity of the solution at this time is $\Lambda\infty_m = V + \Lambda_{m,+} + V_- \Lambda_{m,-}$ (4)

Where $\Lambda_{m,+}$ and $\Lambda_{m,-}$ respectively, positive and negative ions of infinite dilution molar conductivity.

According to the ionization theory, it can be assumed that the ionization degree α of the weak electrolyte is equal: $\alpha = \Lambda_m/\Lambda\infty_m$ (5).

3. Weak Electrolyte Ionization Equilibrium Constant: Weak Electrolyte AB Ionization Equilibrium Constant: $K^{\theta} = (C\alpha^2)/C^{\theta}(1-\alpha)$. Therefore, the value of K^{θ} can be obtained by experimentally measuring α. Substituting (4) into (6) yields

$K^{\theta} = C(\Lambda^{\infty}_m)^2/\Lambda^{\infty}_m C^{\theta}(\Lambda^{\infty}_m-\Lambda_m)$ or $C\Lambda_m = (\Lambda^{\infty}_m)^2 K^{\theta}C^{\theta}1/\Lambda_m - \Lambda^{\infty}_m K^{\theta}C^{\theta}$, (7)

plot $C\Lambda_m$ to $1/\Lambda_m$, the slope of the straight line is $(\Lambda^{\infty}_m)^2 K^{\theta}C^{\theta}$, if you know Λ^{∞}_m value, K^{θ} can be calculated.

Step 1. Turn on the conductivity meter switch, warm-up 5min.

Step 2. Determination of KCl solution conductivity.

Step 3. Determination of HAc Solution Conductivity.

Experiment 6. **The determination of turbidity of water.**

Turbidity is a water quality indicator that refers to the obstruction degree that occurs when the light pass through the suspended solids in water

The suspended solids include soil, silt, micro granular organic matter, inorganic matter, plankton, etc.

Experiment: Directly measure turbidity of water sample using the turbidimeter

Experiment 7. **The determination of SUVA.**

Equipment

- UV-spectrophotometer
- 0.45 μm microfiltration membrane

Step 1. The determination of UV254 using UV-spectrophotometer.

Step 2. Filtering the water sample prior to determination of dissolved organic carbon.

Step 3. Calculating SUVA according to equation SUVA=UV254/DOC*100.

Report content

Calculation of total alkalinity and phenolphthalein alkalinity

	First	Second	Third	Average
V_1 (mL)				
PA($CaCO_3$, mg/L)				
V_2 (mL)				
TA($CaCO_3$, mg/L)				

Calculation of acidity of water

	First	Second	Third	Average
V1 (mL)				
MOA($CaCO_3$, mg/L)				
V2 (mL)				
TA ($CaCO_3$, mg/L)				

Calculation of hardness

Volume (ml)	**1**	**2**	**3**
Sample			
Titration			

Average total hardness=$\frac{c_{EDTA} \times V_{EDTA}}{V_{sample}} \times 1000$

Determination of HCI solution pH:

C/(mol·L^{-1})	pH			
	First	**Second**	**Third**	**Average**
1.00				
0.10				
0.01				
0.001				
0.0001				

Determination of NaOH solution pH:

C/(mol·L^{-1})	pH			
	First	Second	Third	**Average**
1.00				
0.10				
0.01				
0.001				
0.0001				

Determination of (KH_2PO_4)solution pH:

C/(mol·L^{-1})	pH			
	First	Second	Third	**Average**
1.00				
0.10				
0.01				
0.001				
0.0001				

Determination of KCl solution conductivity:

C/(mol·m^{-3})	**κ** (S·m-1)			
	First	Second	Third	**Average**
10.00				
5.00				
2.50				
1.25				
0.625				

Determination of HAc solution conductivity:

C/(mol·m^{-3})	**κ** (S·m-1)			
	First	Second	Third	**Average**
0.093				
0.0465				
0.02325				
0.011625				

Turbidity:

sample	**1**	**2**	**3**	**4**	**5**
NTU					

SUVA:

sample	**1**	**2**	**3**	**4**	**5**
UV254(cm^{-1})					
DOC (mg/L)					
SUVA					

Discussion issues:

1. What substances cause the alkalinity of water?
2. What kinds of acidity can be distinguished in natural water?
3. What substances cause availability of free and aggressive carbon acid in water?
4. What is the active water reaction?
5. What water indicators characterize dry residue and losses of residue at the calcination?
6. How to determine the content of organic substances in samples of natural water?
7. What total content of salts allows to recommend water for drinking?
8. What indicator of water quality is determined by the Kubel's method?
9. The availability of which impurities in water characterizes the value of permanganate oxidation?

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2 Analytical procedures

2.1 Determination of SS, BOD, COD of natural water.

Lab purpose

The aim of work is to learn standard methods of the evaluation of salt content and organic substances content in natural origins of water supply.

Theory

The quantity of salts, dissolved in natural waters, can be determined by dry residue and losses at calcination. The dry residue is formed from the evaporation of some water volume, filtrated previously through the paper filter. Filtrate consists of mineral salts and non-volatile organic substances. The organic part of dry residue of water is determined by residue losses at calcination process. The data about organic substances content in investigated water can be obtained higer than the real magnitude if dissolved salts contain nitrogen, carbon etc. The water is considered fresh, if it usually contents of 1000 mg/L of dissolved salts.

Chemical Oxygen Demand (COD) test determines the oxygen requirement equivalent of organic matter that is susceptible to oxidation by means of a strong chemical oxidant. It is an important, rapidly measured (COD) as indicator of measuring organic strength for streams and polluted water bodies. The test can be related empirically to BOD, organic carbon or organic matter in samples from a specific source taking into account its limitations. The test is useful in studying performance evaluation of wastewater treatment plants and monitoring relatively polluted water bodies. COD determination has advantage over BOD determination. COD results can be obtained in 3 - 4 hrs as compared to 3 – 5 days required for BOD test. Further, the test is relatively easy, precise, and is unaffected by interferences as in the BOD test. The intrinsic limitation of the test lies in its inability to differentiate between the biologically oxidisable and biologically inert material and to find out the system rate constant of aerobic biological stabilization.

Equipment and reagents

Equipment: water bath; porcelain cups; conic bulbs; pipettes; paper filters; funnels; burettes; analytic balances; dry wardrobe; muffle furnace; desiccator.

Reactants: sulfuric acid solution (1:2) (one volume of H_2SO_4 96 % mas. and two volumes of distilled water); 0,01 M solution of potassium permanganate; 0,01 M solution of oxalate acid.

Tasks performance order

Experiment 1. **The determination of dry residue in samples of natural water.**

This determination is usually conducted in a day of picking the sample. Water is filtrated through the paper filter. Porcelain cup is dried to the constant mass, cooled and weighed on analytical balances. Filtrated water is evaporated on water bath, filled by distilled water (100 – 150 cm^3). The cup with dry residue is dried at 100 – 150 ^{0}C to the constant mass, cooled and weighed.

The content of dry residue is calculated by the formula:

$$X = \frac{(m_1 - m) \cdot 100}{V},$$

where X – the content of dry residue, mg/L; m – the mass of cup, mg; m_1 – the mass of cup with dry residue, mg; V – volume of water sample, cm^3.

Experiment 2. **The determination of losses at the calcination of dry residue.**

For the determination of this losses, the dry residue, obtained in previous experiment, is calcined in muffle furnace at the temperature 600 ^{0}C for 1 hour, cooled in desiccator and the cup weighed on analytic balances. Losses are calculated by the formula:

$$X_1 = \frac{(m_2 - m) \cdot 100}{V},$$

where X_1 – the content of calcined sample, characterizing mineral impurities in water, mg/L; m_2 – the mass of cup with residue after calcination, mg.

The content of organic part of impurities is found by the formula:

$$X_2 = X - X_1,$$

where X_2 – the content of organic impurities in water sample, mg/L.

Experiment 3**. The determination of permanganate oxidation in natural water (Kubel's method).**

The water sample (100 cm^3), picked by pipette or volumetric flask, is poured to conic bulb with glass pellets on the bottom, diluted sulfuric acid (5 cm^3) and 10 cm^3 of 0,01 M solution of potassium permanganate is added. The bulb must be heat-resistant. The bulbs content is achieved to boiling. It is boiled exactly 10 min. The 0,01 M solution of oxalate acid (10 cm^3) is added to the bulb with solution. Heated solution is titrated by 0,01 M solution of potassium permanganate to pale pink color. The temperature of the sample shouldn't be less than 80 ^{0}C. Then 10 cm^3 of 0,01 M oxalate acid solution is poured to the same bulb to another head liquid

and titrated by 0,01 M solution of potassium permanganate. The color shouldn't disappear for one minute.

The permanganate oxidation is calculated by the formula:

$$X_3 = \frac{(V_1 - V_2) \cdot 0{,}08 \cdot 1000}{V},$$

where X_3 – the permanganate oxidation of water, mg of O_2 on 1 L of water; V_1 – total content of 0,01 M potassium permanganate solution, taken for the titration, cm^3; V_2 – volume of permanganate solution, taken for the titration of oxalate acid (10 cm^3, the second titration), cm^3; V – volume of water sample, cm^3; 0,08 – oxygen quantity, responding by 1 cm^3 of 0,01 M potassium permanganate solution, mg. (If the calculation of oxidation is in milligrams of the permanganate per 1 L of water, it's necessary to use 0,32 instead of 0,08 – the equivalent of potassium permanganate, responding by 0,01 M solution).

Attention! The determination should be repeated, if water sample will become fulvous or transparent during boiling.

Experiment 4. **Chemical Oxygen Demand (COD).**

Chemical oxygen demand (COD) is a measure of the capacity of water to consume oxygen during the decomposition of organic matter and the oxidation of inorganic chemicals such as ammonia and nitrite. COD measurements are commonly made on samples of waste waters or of natural waters contaminated by domestic or industrial wastes. Chemical oxygen demand is measured as a standardized laboratory assay in which a closed water sample is incubated with a strong chemical oxidant under specific conditions of temperature and for a particular period of time. A commonly used oxidant in COD assays is potassium dichromate $(K_2Cr_2O_7)$ which is used in combination with boiling sulfuric acid (H_2SO_4). Because this chemical oxidant is not specific to oxygen-consuming chemicals that are organic or inorganic, both of these sources of oxygen demand are measured in a COD assay.

Chemical oxygen demand is related to biochemical oxygen demand (BOD), another standard test for assaying the oxygen-demanding strength of waste waters. However, biochemical oxygen demand only measures the amount of oxygen consumed by microbial oxidation and is most relevant to waters rich in organic matter. It is important to understand that COD and BOD do not necessarily measure the same types of oxygen consumption. For example, COD does not measure the oxygen-consuming potential associated with certain dissolved organic compounds such as acetate. However, acetate can be metabolized by microorganisms and would therefore be detected in an assay of BOD. In contrast, the oxygen-consuming potential of cellulose is not measured during a short-term BOD assay, but it is measured during a COD test.

Open Reflux method

I. Principle

The open reflux method is suitable for a wide range of wastes with a large sample size. The dichromate reflux method is preferred over procedures using other oxidants (e.g. potassium

permanganate) because of its superior oxidizing ability, applicability to a wide variety of samples and ease of manipulation. Oxidation of most organic compounds is up to 95-100% of the theoretical value.

The organic matter gets oxidized completely by potassium dichromate $K_2Cr_2O_7$ with silver sulphate as catalyst in the presence of concentrated H_2SO_4 to produce CO_2 and H_2O. The excess $K_2Cr_2O_7$ remained after reaction is titrated with ferrous ammonium sulphate $Fe(NH_4)_2(SO_4)_2$. The dichromate consumed gives the oxygen (O_2) required for oxidation of organic matter. The chemical reactions involved in the method are as under:

a) $2K_2Cr_2O_7 + 8H_2SO_4 \rightarrow 2K_2SO_4 + 2Cr_2(SO_4)_3 + 8H_2O$
b) $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$
c) $Cr_2O_7^{--} + 6\ Fe^{++} + 14H^+ \rightarrow 6Fe^{+++} + 2\ Cr_3^+ + 7H_2O$

II. Apparatus and equipment

a. 250 or 500mL Erlenmeyer flask with standard (24/40) tapered glass joints.

b. Friedrich's reflux condenser (12 inch) with standard (24/40) tapered glass joints.

c. Electric hot plate or six-unit heating shelf.

d. Volumetric pipettes (10, 25, and 50mL capacity).

e. Burette, 50mL with 0.1mL accuracy.

f. Burette stand and clamp.

g. Analytical balance, accuracy 0.001 g.

h. Spatula.

i. Volumetric flasks (1000 mL capacity).

j. Boiling beads, glass.

k. Magnetic stirrer and stirring bars.

III. Reagents and standards

a. Standard potassium dichromate solution, 0.25N (0.04167 M): Dissolve 12.259 g $K_2Cr_2O_7$ dried at 103°C for 24h in distilled water and dilute to 1000 mL. Add about 120mg sulphamic acid to take care of 6 mg/L NO_2 – N.

b. Sulphuric acid reagent: Add 10g of Ag_2SO_4 to 1000mL concentrated H_2SO_4 and let stand for one to two days for complete dissolution.

c. Standard ferrous ammonium sulphate approx. 0.25N (0.25M): Dissolve 98g $Fe(NH_4)_2(SO_4)_2.6H_2O$ in about 400mL distilled water. Add 20 mL concentrated H_2SO_4 and dilute to 1000 mL.

d. Ferroin indicator: Dissolve 1.485 g 1,10-phenanthroline monohydrate and 695mg $FeSO_4.7H_2O$ in distilled water and dilute to 100 mL.

e. Mercuric Sulphates: $HgSO_4$, crystals, analytical grade

f. Potassium hydrogen phthalate (KHP) Standard: Dissolve 425 mg lightly crushed dried potassium hydrogen phthalate $(HOOC.C_6H_4.COOK)$ in distilled water and dilute to 1000 mL.

This solution has a theoretical COD of 500 µg O_2/mL. This solution is stable when refrigerated, up to 3 months in the absence of visible biology.

IV. Sample collection, preservation and storage

Preferably collect samples in glass bottles. Homogenize samples containing settleable solids. If there is delay in collection and analysis, preserve sample by acidification to pH ≤ 2 using concentrated H_2SO_4. Samples can be preserved for maximum 7 days.

V. Calibration

Since the procedure involves chemical oxidation of organic matter by potassium dichromate as oxidizing agent, which is a primary standard, calibration is not required. For standardization of ferrous ammonium sulphate, dilute 10mL standard $K_2Cr_2O_7$ to about 100 mL. Add 10mL of concentration H_2SO_4 and allow it to cool. Titrate with ferrous ammonium sulphate (FAS) is to be standardized using 2 - 3 drops of ferroin indicator. (mL $K_2Cr_2O_7$) (0.25)

Normality of FAS =

mL FAS required

The deterioration of FAS can be decreased if it is stored in a dark bottle.

VI. Procedure

Sample preparation: All samples high in solids should be blended for 2 minutes at high speed and stirred when an aliquot is taken for analysis. Select the appropriate volume of sample based on expected COD range, e.g. for COD range of 50-500 mg/L take 25 - 50 mL of sample. Sample volume less than 25 mL should not be pipetted directly, but serially diluted and then a portion of the diluted sample taken. Dilution factor should be incorporated in calculations.

a. 500 mL of sample diluted to 1000 mL = 0.5 mL sample/mL of diluent, 50 mL = 25 mL of sample.

b. 100 mL of sample diluted to 1,000 mL = 0.1 mL sample/mL diluent, 50mL of diluent = 5 mL of sample.

Reflux of samples:

a. Place 0.4 g $HgSO_4$ in a 250 mL reflux sample.

b. Add 20mL sample or an aliquot of sample diluted to 20 mL with distilled water. Mix well.

c. Add clean pumic stones or glass beads.

d. Add 10 mL 0.25N (0.04167M) $K_2Cr_2O_7$ solution and mix.

e. Add slowly 30 mL concentrated H_2SO_4 containing Ag_2SO_4 mixing thoroughly. This slow addition along with swirling prevents fatty acids to escape due to generation of high temperature. Alternatively attach flask to condenser with water flowing and then add H_2SO_4 slowly through condenser to avoid escape of volatile organic substance due to generation of heat.

f. Mix well. If the colour turns green, either take fresh sample with lesser aliquot or add more potassium dichromate and acid.

g. Connect the flask to condenser. Mix the contents before heating. Improper mixing will result in bumping and blow out of flask content.

h. Reflux for a minimum of 2 hours. Cool and then wash down condenser with distilled water.

i. Disconnect reflux condenser and dilute the mixture to about twice its volume with distilled water. Cool to room temperature and titrate excess $K_2Cr_2O_7$ with0.1M FAS using 2-3 drops of ferroin indicator. The sharp colour change from blue green to reddish brown indicates end-point or completion of the titration. After a small time, gap, the blue-green colour may reappear. Use the same quantity of ferroin indicator for all titrations.

j. Reflux blank in the same manner using distilled water instead of sample.

Alternate procedure for low COD samples less than 50 mg/L: Follow similar procedure with two exceptions (a) use standard 0.025N (0.004167M) $K_2Cr_2O_7$ and (b) titrate with standardize 0.025M FAS. The sample volume should be 5mL. Exercise extreme care with this procedure because even a trace of organic matter on the glassware or from the atmosphere may cause gross errors. Compute amount of $HgSO_4$ to be added based on chloride concentrations. Carry blank reagent through the same procedure.

VII. Calculations

COD as mg/L = (a –b) x N x 8000 / mL sample

Where, a = mL FAS used for blank

b = mL FAS used for sample

N = normality of FAS

8000 = Milieq. wt. of O_2 x 1000

VIII. Precision and Bias

Precision and bias: A set of synthetic samples containing potassium hydrogen phthalate with a COD of 200 mg/L was analyzed in many labs with standard deviation of 13 mg/L in absence of chloride.

Sources of Error:

a. The largest error is caused by using a non-homogeneous sample. Every effort should be made to blend and mix the sample so that solids are never excluded from any aliquot.

b. Use volumetric flasks and volumetric pipettes with a large bore.

c. The $K_2Cr_2O_7$ oxidising agent must be precisely measured. Use a volumetric pipette and use the same one each time if possible.

d. When titrating, be certain that the burette is clean and free of air bubbles.

e. Always read the bottom of the meniscus and position the meniscus of eye level.

Carry distilled water blank through a same procedure to nullify impurities if any. A standard solution of glucose or potassium acid phthalates should be checked for precision and accuracy every fortnight. Duplicate analysis is preferred.

Method Sensitivity:

1 Standard procedure is precise and accurate for COD of 50 mg/L or more

2 For low COD more sample volume and the dilute reagents are used

3 Interference by chloride needs to be handles very carefully to get accurate results

IX. Interferences

Fatty acids, straight chain aliphatic compounds, aromatic hydrocarbons, chlorides, nitrite and iron interfere in the estimation. The interference caused by chloride can be eliminated by the addition of mercuric sulphate to the sample prior to the addition of other reagents. About 1.0g of mercuric sulphate is adequate to complex 100mg chloride ions in the sample in the form of poorly ionized soluble mercuric chloride complex. Addition of Ag_2SO_4 to concentrated H_2SO_4 as a catalyst stimulates the oxidation of straight chain aliphatic and aromatic compounds. Nitrite nitrogen exerts a COD of 1.14 mg/mg $NO_2 - N$.

Sulphuric acid at the rate of 10mg/mg $NO_2 - N$ may be added to $K_2Cr_2O_7$ solution to avoid interference caused by $NO_2 - N$. Aromatic hydrocarbons and pyridine are not oxidised under any circumstances. Volatile organic compounds will react in proportion to their contact with the oxidant. For complete oxidation of organic matter, it is necessary to take volumes of Sulphuric acid and sample plus potassium dichromate in 3:2:1 ratio. However, to maintain the ratio, the volumes and strength of oxidant/sample may suitable be varied.

X. Warnings

In carrying out the procedures, use proper safety measures, including protective clothing, eye protection and a fume hood. Reagents containing heavy metals ($HgSO_4$ and Ag_2SO_4) should be disposed of as toxic wastes. Use of such chemicals should be minimized whenever feasible.

XI. Pollution prevention and waste minimization

Since hazardous chemicals like silver and mercury salts, Sulphuric acid, dichromate are used in the test, the quantity of such chemicals can be minimized by selecting minimum suitable sample size. The liquid waste generated should be treated as hazardous waste. Adequate dilution of such waste before final disposal is essential.

Closed reflux (titrimetric and colorimetric) method using COD digester

I. Principle

The closed reflux (titrimetric and colorimetric) method using metallic salt reagents are more economical but require homogenization of samples to obtain reproducible results. This method is conducted with ampules and culture tubes with pre-measured reagents which are available commercially. Moreover, for performing the tests, instructions furnished by the manufacturer

are to be followed. Measurement of sample volume and reagent volume are critical. This method is economical in the use of metallic salt reagents and generates a smaller quantity of hazardous wastes.

The principle of the oxidation reaction is similar to open reflux method. Volatile organic compounds are more completely oxidized in a closed system because of longer contact time with oxidants. Digestion vessels with premixed reagents are also available from commercial suppliers.

II. Apparatus and equipment

a. Digestion vessels with premixed reagents and other accessories commercially available.

b. Borosilicate culture tubes 16 x 100 mm, 20 x 150 mm or 25 x 150 mm with TF and lined screw caps.

c. Borosilicate ampule 10 mL cap – 19 to 20 mm diameter.

d. Block heater to operate at 150 ± 2°C with holes to accommodate digestion vessels. Care for culture tube caps required.

e. Micro-burette.

f. Ampule sealer.

III. Reagents and standards

Standard potassium dichromate digestion solution 0.01667M: Dissolve 4.903 g $K_2Cr_2O_7$, primary standard grade, previously dried at 150 ℃ for 2 hours in 500 mL distilled water, add

167 mL conc. H_2SO_4 at the rate of 5.5g Ag_2SO_4/kg H_2SO_4. Let stand 1 to 2 d to dissolve and mix.

Ferroin indicator solution: Dissolve 1.485 g 1,10-phenanthroline monohydrate and 695 mg $Fe(SO_4)_2.7H_2O$ in distilled water and dilute to 100mL. This indicator solution may be purchased already pre

Standard ferrous ammonium sulphates (FAS) titrant, approximately 0.1M: Dissolve 39.2g $Fe(NH_4)_2(SO_4)_2.6H_2O$ in distilled water. Add 20mL concentrated H_2SO_4, cool and dilute to100mL. Standardise this solution daily against standard $K_2Cr_2O_7$.

IV. Calibration

Dilute 5mL standard $K_2Cr_2O_7$ digestion mixture to about 100mL. Titrate with FAS using 0.1 to 0.15mL. (2 to 3 drops) ferroin indicator.

Normality of FAS solution

Volume of 0.01667 M $K_2Cr_2O_7$ solution treated, mL = x 0.1

Volume FAS used in titration, mL

V. Procedure

a. Treatment of sample with COD of > 50mg/L.

b. Blend sample if the suspended matter is present.

c. Wash culture tubes and caps with 20% H_2SO_4 before first use.

d. Refer the following to select analytical parameters for proper sample and reagent volume.

e. Place sample in culture tube or ampule.

f. Add digestion mixture.

g. Carefully run sulphuric acid reagent down inside of vessel.

h. Tightly cap the tubes or seal ampules. Invert several times for proper mixing.

i. Place tubes or ampules in preheated reaction block digestor.

j. Reflux for 2h at 150°C behind a protective shield.

k. Cool to room temperature.

l. Remove caps and put TFE covered magnetic stirrer.

m. Titrate while stirring with FAS using 1 or 2 drops of ferrous indicator.

n. The end points are from blue-green to reddish brown.

o. Reflux and titrate blank in a similar way with distilled water.

VI. Calculation

COD as mg O_2/L = (A – B) x M x 8000 / ml sample

Where:

A = mL FAS used for blank

B = mL FAS used for sample

M = molarity of FAS, and

8000 = milli equivalent weight of oxygen x 1000 mL/L

VII. Precision and Bias

A set of synthetic containing potassium hydrogen phthalate and NaCl was tested by 74 laboratories. At a COD of 200 mg O_2/L in the absence of chloride, the standard deviation was ± 13 mg/L (coefficient of variation, 6.5%). At COD of 160 mg O_2/L and 100 mg Cl/L, the standard deviation was ± 14 mg/L (coefficient of variation, 10.8%).

For quality control refer Open Reflux Method.

a. Preferable analyze duplicate samples.

b. Proper homogenization is essential for reproducible results.

c. Make volumetric measurement as accurate as possible.

d. Use class-A volumetric flask.

Table 1: Sample and reagent quantities for various digestion vessels

Culture Tubes:	Quantity of samples, g			
16 x100 mm	5.00	1.50	3.5	7.5
20 x 150 mm	2.50	3.00	7.0	15.0
25 x 125 mm	10.00	6.00	14.0	30.0
Standard10-mL Ampules	2.50	1.50	3.5	7.5

Report content

COD and BOD of different samples of water

Sample	**COD, mg O_2 / L**		**BOD, mg O_2 / L**
	Permanganate	**Dichromate**	
1			
2			
3			
4			

Discussion issues:

1. What water indicators characterize dry residue and losses of residue at the calcination?
2. How to determine the content of organic substances in samples of natural water?
3. What total content of salts allows to recommend water for drinking?
4. What indicator of water quality is determined by the Kubel's method?
5. The availability of which impurities in water characterizes the value of permanganate oxidation?

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2.2 Biochemical Oxygen Demand

Theory

As defined by the DIN EN 1899-1 the Biochemical Oxygen Demand (BOD) is the mass per unit volume of oxygen for the oxidation of biochemically oxidizable substances contained in 1 L of sample water in n days, in general, n = 5; BOD_5, possible n = 7) summarily consumed in the metabolic activity of a corresponding microbiocenosis at 20 ° C.

The ratio of the theoretical biological oxygen demand, to chemical oxygen demand (COD), characterizes the degradability of the ingredients of the water to be examined.

The BOD_5 / COD ratio is changing during wastewater treatment as follows:

Inflow wastewater treatment plant	BOD_5 : COD: about 1: 2
Effluent secondary clarifier	BOD_5 : COD: about 1: 4

The dilution method is the officially approved method of measurement. Here shares of wastewater sample are diluted with a specially prepared dilution water (see below). The mixtures are incubated for 5 days at 20 ° C in dark environment.

BOD_5 is calculated from the decrease in oxygen concentration in the dilutions as well as in dilution water (O_2 consumption).

The determination of BOD by a manometric method is easier by measuring the oxygen consumption via pressure measurement (see below).

The determination of the BOD_5 should only achieve on the oxygen demand for the oxidation of carbon compounds. Nitrification causes an additional, poorly reproducible oxygen consumption and is undesirable in the BOD determination. The addition of an inhibiter delays the start of nitrification; usually Allylthiourea (ATU) is used for this purpose.

Dilution method of BOD_5 determination

Experimental Procedure

Dilution water

The dilution water is composed as follows:
Adding 1 ml of the below mentioned salt solutions to approx. 0.5 l of deionized water. To this solution, 5 ml inoculating water (domestic wastewater - either sedimented or filtrated effluent of primary clarifier) are added.

At least 1 h aeration at 20 °C: The O_2 concentration should be at least 8 mg / l. The water may not be supersaturated with oxygen, therefore leave the solution in an open tank for 1 h. This solution is to be used within 24 h after preparation.

Salt solutions

Phosphate buffer solution, pH 7.2

Magnesium sulfate heptahydrate solution 22.5 g/L

A solution of calcium chloride 27.5 g/L

Iron-(III)-chloride hexahydrate solution 0.25 g/L

- The sample is to be homogenized with an Ultra-Turrax for 30 seconds.
- A defined volume (see below) of homogenized wastewater sample is to be filled into a graduated cylinder.
- Add 2 ml ATH solution (c_{ATH} = 1 g/L)
- Filling up to 1l with dilution water and mix.
- 3 sample is to be prepared for each dilution series:

Effluent primary clarifier: (expected BOD_5: 100-300 mg/L):

Sample volume: 20, 30, 50 ml

Effluent secondary clarifier: (expected BOD_5: 5-10 mg / L)

Sample volume: 200, 300, 500 ml

Distribute the content of the glass cylinder on 3 Reagent bottles and seal immediately with a plug - small volumes of liquid should leak out to prevent trapped air bubbles.

In addition, a blank sample is to be applied: Fill measuring cylinder with 1 L of dilution water and add 2 ml ATU-solution, also spread over 3 reagent bottles and closed.

In one bottle of each dilution series, the initial oxygen content is to be measured. The remaining 2 bottles of each dilution series and the blank value at 20°C are thermostated in the incubator for 5 or 7 days. After this time the final oxygen is to be measured and the BOD-value is to be calculated.

Test results

Determining the BOD value according to the formula:

$$BOD_n = \left((Z_p - Z_V) \times \frac{d}{e} \right) + Z_V$$

With BOD_n = Biological oxygen consumption after n days [mg/L O_2]
Z_p = O_2-consumption of the diluted wastewater sample [mg / L]
Z_V = O_2-consumption of dilution water [mg / L]
d = sum of sample and dilution filled in the mixing tank [ml]
e = water sample charged into the mixing tank [ml]

The BOD value is to be indicated as an average of the individual dilutions. The dilution water shall have an oxygen consumption of 0.5 to 1.5 mg/L.

Manometric method of BOD5 determination

Theory

The manometric BOD determination with the OxiTop system supplied by WTW, based on a pressure measurement (differential measurement). The data acquisition via electronic piezoresistive pressure sensors, that are integrated into the OxiTop measuring head. This measuring head is so mounted on the measuring flask, that the sample contained therein is completely sealed from the atmosphere.

On top of the sample is an airspace, which oxygen content is used for the oxygen supply of the microorganisms in the sample. The released CO_2 is absorbed in the airspace by potassium or sodium hydroxide. By this means, a pressure loss happens which is proportional to the oxygen consumption of the microorganisms. This pressure loss is read as a BOD-value at the measuring head.

Accordingly, to the expected BOD, the water sample volumes (homogenized) used is listed in the table below:

Table 1: Expected BOD(mg/L) range for corresponding volume (ml)

measuring range BOD_5 (mg / l)	Filling volume (ml)	conversion factor (Multiplied by the indication value)
0 - 35	432	1
0 - 70	365	2
0-175	250	5
0-350	164	10
0-700	97	20
0-1750	43.5	50
0-3500	22.7	100

Experimental Procedure

The corresponding sample volume is filled into a brown glass bottle (500 ml). ATU from the stock solution (c = 1 g/L) is added to the sample with the target to establish an ATU-concentration of about 2 mg / l. In the bottle, a magnetic stirrer is given.

A rubber receptacle is filled with 2 NaOH pellets and placed on the bottle neck. Thereafter, the OxiTop measuring head is screwed onto the bottle firmly.

For further information see instructions, "Operation OxiTop." (In chapter "Forms")

It is recommended to establish 2 bottles per sample.

Fig 1: Brown glass bottles with sample

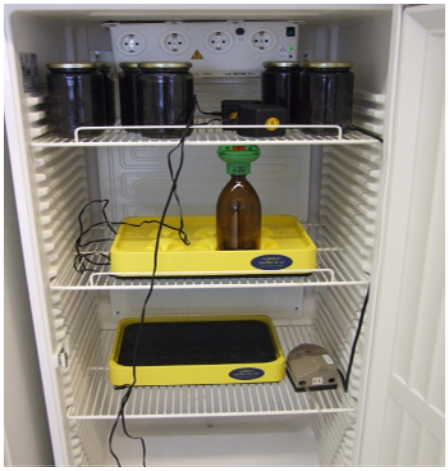


Fig 2: Thermostated oven (20 ° C) (BOD cabinet)

Experimental sheets :

Table 2: Datasheet for evaluating the BOD 5 dilution method

Datenblatt zur Auswertung der BSB_5-Bestimmung nach der Verdünnungsmethode

Bezeichnung der Probe	BSB_5 Flaschen Nr.	Wasserprobe im Mischgefäß (e)	Wasserprobe und Verdünnungs-wasser (d)	Bezeichnung	Sauerstoffkon-zentration $c\ (O_2)_{Mittel}$	O_2 - Zehrung (Z_p bzw. Z_v) $=c\ (O_2)_A - c\ (O_2)_{Mittel}$	$BSB_5 = d/e * (Z_p - Z_v) + Z_v$	Bemerkungen
--	--	ml	ml	--	mg O_2/l	mg O_2/l	mg O_2/l	--
Verdünnungs-wasser				$c\ (O_2)_A$ $c\ (O_2)_{E1}$ $c\ (O_2)_{E2}$		Z_v=		
Probe 1				$c\ (O_2)_A$ $c\ (O_2)_{E1}$ $c\ (O_2)_{E2}$		Z_p=		
Probe 2				$c\ (O_2)_A$ $c\ (O_2)_{E1}$ $c\ (O_2)_{E2}$		Z_p=		
Probe 3				$c\ (O_2)_A$ $c\ (O_2)_{E1}$ $c\ (O_2)_{E2}$		Z_p=		

Erläuterungen:

- $c\ (O_2)_A$: Anfangssauerstoffgehalt
- $c\ (O_2)_{E1}$: Endsauerstoffgehalt in Flasche 1
- $c\ (O_2)_{E2}$: Endsauerstoffgehalt in Flasche 2
- $c\ (O_2)_{Mittel}$: Mittelwert der Endsauerstoffkonzentrationen in den Flaschen 1 und 2
- Voraussetzung für die Auswertung $c\ (O_2)_{E1}$, $c\ (O_2)_{E2}$ > 2 mg/l
- Sauerstoffzehrung in der Probe Z_p > 2 mg/l
- Sauerstoffzehrung im Verdünnungswasser Z_v : 0,5 bis 1,5 mg/l

Table 3: Chart sheets for entering the BOD values of the Manometric Method.

WTW

Diagrammbogen für BSB_5-Meßgeräte / ***Diagram Sheet for BOD_5 Meters***

Name / *name*: ..... Datum / *date*: .....

BSB / *BOD* / *DBO* (mg/l)	Füllvol. / *Filling Vol.* (ml)	Faktor / *Factor*	BSB / *BOD* / *DBO* (mg/l)	Füllvol. / *Filling Vol.* (ml)	Faktor / *Factor*
0 ... 40	432	1	0 ... 400	164	10
0 ... 80	365	2	0 ... 800	97	20
0 ... 200	250	5	0 ... 2000	43.5	50

Probe / *Sample*	1	2	3	4	5	6
Entnahmestelle / *Place of Sampling*						
Meßbereich / *Measuring Range*						
Füllvolumen / *Filling Volume*						
Meßbeginn / *Start of Measurement*						
Verdünnung / *Dilution*						
Faktor / *Factor*						
Meßwert (Digit) / *Reading (digit)*						
BSB_5-Wert / BOD_5 *Value*						
Mittelwert BSB_5 / *Average* BOD_5						

Bemerkungen / *Remarks*:

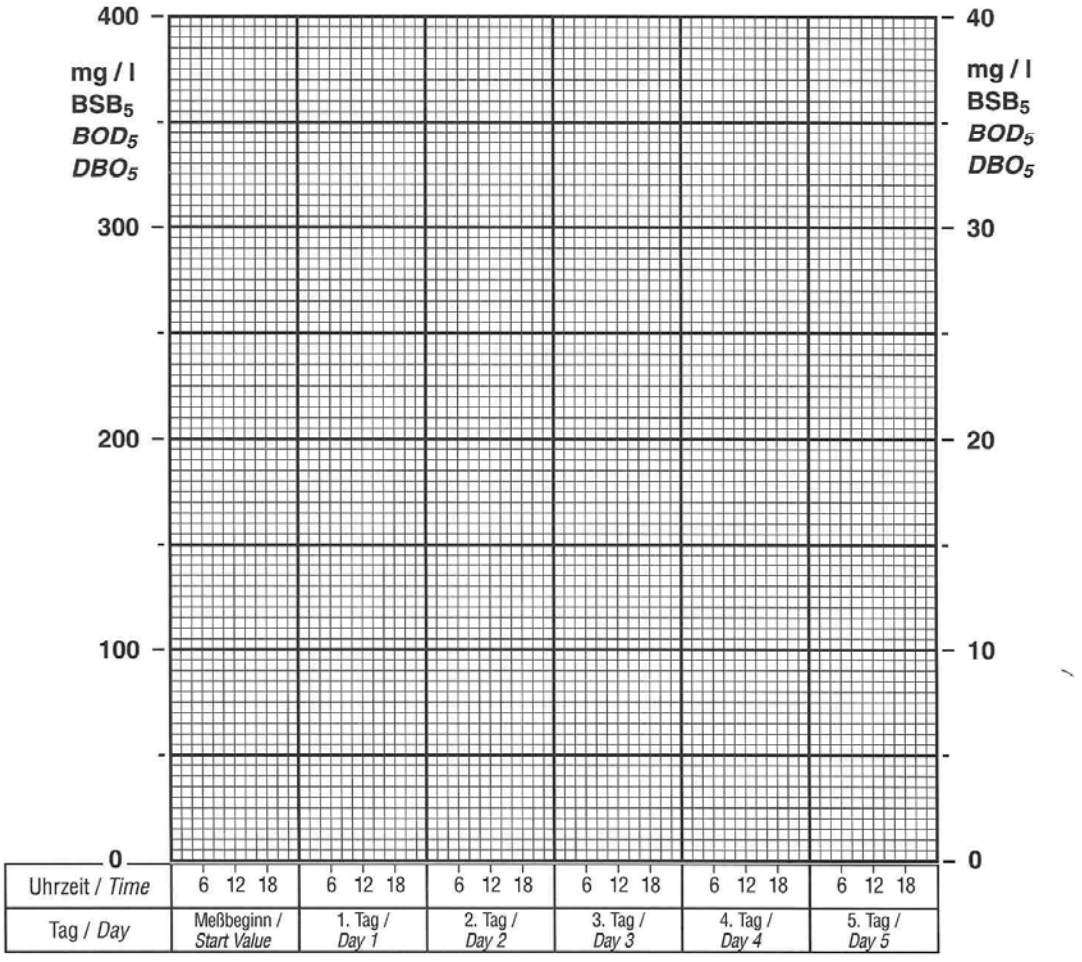


Table 4: Quick Guide OxiTop measuring heads.

OxiTop® Betrieb

Probevolumen wählen

Abschätzung des für die Abwasserprobe zu erwartenden BSB5-Werts:
Erwarteter BSB5-Wert ~ 80 % des CSB-Werts
Entsprechenden Meßbereich in der nebenstehenden Tabelle suchen und zugehörige Werte für Probevolumen und Faktor entnehmen.

Probevolumen (ml)	Meßbereich (mg/l)	Faktor
432	0 - 40	1
365	0 - 80	2
250	0 - 200	5
164	0 - 400	10
97	0 - 800	20
43,5	0 - 2000	50
22,7	0 - 4000	100

Probenvorbereitung

Siehe folgende WTW-Applikationsberichte:
- WTW-Applikationsbericht 895230: "BSB-Messung in häuslichen Abwässern"
- WTW-Applikationsbericht 895231: "BSB-Messung in organisch stark belasteten Abwässern"
- WTW-Applikationsbericht 895232: "BSB-Messung bei Anwesenheit hemmender oder toxischer Stoffe"

Messung

Hinweise: Zum Abmessen des Meßgutvolumens werden üblicherweise Überlaufmeßkolben oder Meßzylinder verwendet.
Das Volumen entsprechend des zu erwartenden Meßwertes auswählen, zu groß gewählte Meßbereiche führen zu ungenauen Ergebnisse. Zum Abschätzen des Meßwertes kann mit etwa 80% des CSB-Wertes gerechnet werden.

- **Probenvorbereitung und Befüllen der Meßflaschen** vgl. folgende Vorschrift: DIN 38409 Teil 52: "Messung der Sauerstoffzehrung" sowie WTW-Applikationsberichte siehe Kapitel "Probenvorbereitung".
- **Meßflasche mit der Wasserprobe vorspülen** - gut austropfen -.
- Erforderliche sauerstoffgesättigte (gut homogenisierte) **Probenmenge gemäß Hinweise genau abmessen.**
- **Magnetrührstäbchen** in die Meßflasche geben.
- In den Flaschenhals einen **Gummiköcher** einsetzen.
- 2 **Natriumhydroxid-Plätzchen** mit einer Pinzette in Gummiköcher legen. (Achtung: Plätzchen dürfen keinesfalls in die Probe gelangen!)
- OxiTop® auf **Meßflasche** direkt aufschrauben (dicht verschließen).

S + M — Messung starten:
S und M gleichzeitig drücken (2 Sekunden) bis Anzeige auf 00 wechselt.

2 sec ⇨ 00 — Anzeige: Gespeicherte Werte sind gelöscht.

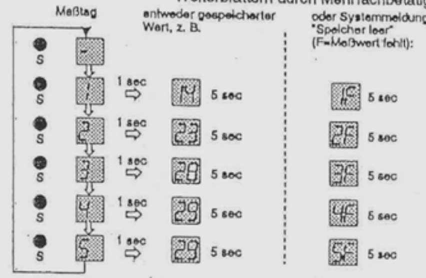
- Meßflasche mit aufgesetztem OxiTop® **fünf Tage bei 20°C inkubieren** (z.B. Thermostatenschrank/-box). Nach Erreichen der Meßtemperatur (frühestens nach 1 Std., spätestens nach etwa 3 Std.; **AutoTemp-Funktion**), beginnt das OxiTop® automatisch mit der Messung des Sauerstoffverbrauchs.
- Während der 5 Tage die Wasserprobe **ständig rühren.**
Das OxiTop® **speichert über 5 Tage automatisch alle 24 Std.** einen Meßwert. Zur Abfrage des aktuellen Meßwertes Taste M drücken.

M — Aktuellen Meßwert anzeigen:
M drücken bis Meßwertanzeige (1 Sekunde)
z.B. 29

Betrieb / Wartung OxiTop®

- Nach Ablauf der 5 Tage die **gespeicherten Meßwerte auslesen.**

S — Gespeicherte Meßwerte auslesen:
S drücken bis Meßwertanzeige (1 Sekunde)
Weiterblättern zum nächsten Tag durch erneutes Drücken der Taste S während der Meßwertanzeige (5 sec). Schnelles Weiterblättern durch Mehrfachbetätigung der Taste S.



- Angezeigten Meßwert in Skalenteilen mit Hilfe folgender Tabelle in den BSB-Wert umrechnen (Skalenteile x Faktor = BSB5 in mg/l):

Probevolumen (ml)	Meßbereich (mg/l)	Faktor
432	0 - 40	1
365	0 - 80	2
250	0 - 200	5
164	0 - 400	10
97	0 - 800	20
43,5	0 - 2000	50
22,7	0 - 4000	100

Störungen

- **Meßbereichsunterschreitungen: Anzeige zeigt Null oder ein zu geringer Meßwert. Die Meßanordnung ist undicht.**
Gummiköcher, Schraubverschluß und Flasche prüfen. Unzureichende Probenvorbehandlung, mangelnde Probenkonservierung. Die Temperatur des Meßgutes war nicht ausreichend angeglichen (< 15°C).
- **Meßbereichsüberschreitungen**
Es wurde ein zu kleiner Meßbereich gewählt. Bei sehr hohen Werten (> 2000 mg/l) empfiehlt sich die Probenvorverdünnung.
Fehlender, mangelnder Nitrifikationshemmstoff (ATH).

Nicht aufgeführt sind verfahrensbedingte Fehler.

Systemmeldungen

Speicher leer (F= Meßwert 1.Tag fehlt)	Meßbereichsunterschreitung < 0 Digit
Batterien wechseln (ca. alle 3 Jahre)	Meßbereichsüberschreitung > 50 Digit

Reinigung der Meßflaschen

- **Keine Desinfektionsmittel** verwenden! (Desinfektionsmittel töten die benötigten Mikroorganismen!)
- **Grobe Verunreinigungen** mechanisch entfernen, z.B. mit einer **Bürste.**
- Die Flaschen mit **klarem Wasser** oder mit **Wasser der nächsten Probe** spülen. (Nach Einsatz von Reinigungsmitteln gründlich spülen! Reinigungsmittelreste können die BSB5-Bestimmung stören!)

3 Unit processes

3.1 Coagulation

Lab purpose

The objectives of this lab work are to estimate the optimum dosage of coagulant (aluminum sulfate or ferric sulfate) for the removal of suspended matter and to investigate the formation of the flocs as a result of aluminum sulfate addition.

Theory

Coagulation and flocculation are important unit processes in water and wastewater treatment plants. The purpose of coagulation/flocculation is to remove suspended matter, turbidity, color and colloidal substances, which cannot be separated from the liquid by sedimentation alone except by the use of reasonably long detention periods. In the coagulation/flocculation process, the chemical reagents (called coagulants) are used to destabilize the suspended and colloidal substances. This form the flocs and increase the floc size. Then, the flocs formed are subsequently removed by sedimentation and/or filtration.

Coagulation involves the addition of chemicals to destabilize the suspended particles, colloidal materials and macromolecules. Coagulants with positive charges, opposite to those of the suspended solids are added to the water to neutralize the negative charges on dispersed non-settable solids, such as clay and organic substances. Thereby, the zeta potentials are reduced to achieve destabilization of particles.

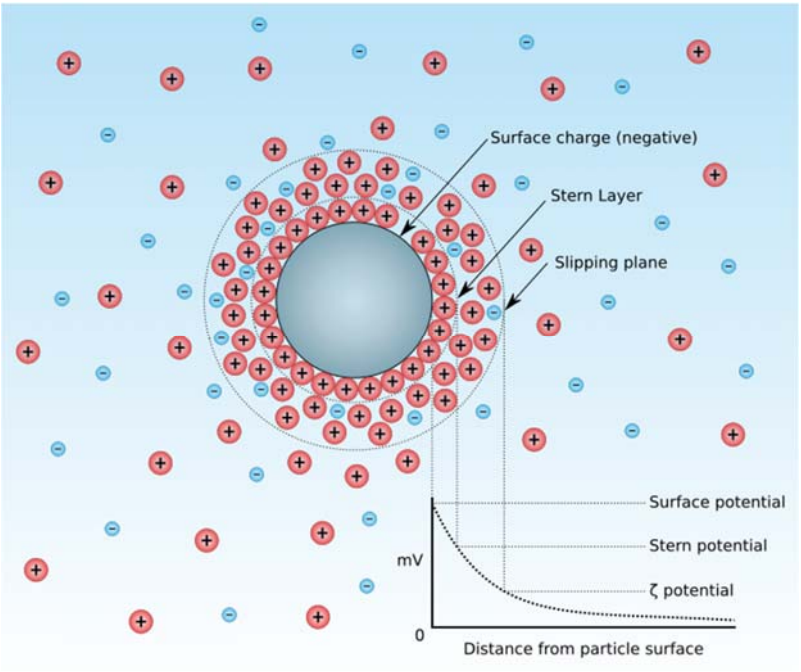


Figure 1: Scheme of emergence micelle.

The destabilization of colloidal particles can be influenced by the double layer compression, adsorption and charge neutralization, entrapment in precipitates (sweep flocculation) and interparticle bridging. The destabilized small-suspended particles are capable of approaching, aggregating and form a cluster. The slightly larger particles formed through this process are called microflocs and are still too small to be visible to the naked eye. A high-energy, rapid-mix to properly disperse the coagulant and promote particle collisions is needed to achieve good coagulation and formation of the microflocs. Over-mixing does not affect coagulation but insufficient mixing will leave this step incomplete. Proper contact time in the rapid-mix chamber is typically 1 to 3 minutes.

Following coagulation, flocculation increases the particle size from submicroscopic microfloc into larger flocs under gentle mixing conditions. Through mild agitation of 20 min to 60 min, collisions of the microflocs and interaction with inorganic polymers formed by the coagulants are cause them to bond together to achieve larger, visible flocs (called macroflocs). The agitation should be gentle, in order to promote floc growth and not to break flocs already formed. After the floc has formed and grown to its most effective size, the water passes through a separation process (sedimentation or filtration) for solids removal.

The commonly used metal coagulants fall into two general categories: those based on aluminum and those based on iron. The aluminum coagulants include aluminum sulfate, aluminum chloride and sodium aluminate. The iron coagulants include ferric sulfate, ferrous sulfate, ferric chloride and ferric chloride sulfate. Other chemicals used as coagulants include hydrated lime and magnesium carbonate.

The effectiveness of aluminum and iron coagulants arises principally from their ability to form multi-charged polynuclear complexes with enhanced adsorption characteristics. The nature of the complexes formed may be controlled by the pH of the system.

When metal coagulants are added to water the metal ions (Al and Fe) hydrolyze rapidly but in a somewhat uncontrolled manner, forming a series of metal hydrolysis species. The efficiency of rapid mixing, the pH and the coagulant dosage determine which hydrolysis species is effective for treatment.

There has been the considerable development of pre-hydrolyzed inorganic coagulants, based on both aluminum and iron to produce the correct hydrolysis species regardless of the process conditions during treatment. These include aluminum chlorohydrate, polyaluminum chloride, polyaluminum sulfate chloride, polyaluminum silicate chloride and forms of polyaluminum chloride with organic polymers. Iron forms include polyferric sulfate and ferric salts with polymers. There are also polymerized aluminum-iron blends.

The principal advantages of pre-polymerized inorganic coagulants are that they are able to function efficiently over wide ranges of pH and raw water temperatures. They are less sensitive to low water temperatures; lower dosages are required to achieve water treatment goals; less chemical residuals are produced; and lower chloride or sulfate residuals are produced, resulting in lower final water TDS. They also produce lower metal residuals.

Pre-polymerized inorganic coagulants are prepared with varying basicity ratios, base concentrations, base addition rates, initial metal concentrations, aging time and aging temperature. Because of the highly specific nature of these products, the best formulation for

a particular water is case specific and needs to be determined by jar testing. For example, in some applications alum may outperform some of the polyaluminum chloride formulations[1]. Polymers are a large range of natural or synthetic, water soluble, macromolecular compounds that have the ability to destabilize or enhance flocculation of the constituents of a body of water.

Natural polymers have long been used as flocculants. For example, Sanskrit literature from around 2000 BC mentions the use of crushed nuts from the Nirmali tree (Strychnos potatorum) for clarifying water – a practice still alive today in parts of Tamil Nadu, where the plant is known as Therran and cultivated also for its medicinal properties. In general, the advantages of natural polymers are that they are virtually free of toxins, biodegradable in the environment and the raw products are often locally available. However, the use of synthetic polymers is more widespread. They are, in general, more effective as flocculants because of the level of control made possible during manufacture.

Important mechanisms relating to polymers during treatment include electrostatic and bridging effects. Figure shows schematic stages in the bridging mechanism. Polymers are available in various forms including solutions, powders or beads, oil or water-based emulsions and the Mannich types. The polymer charge density influences the configuration in solution: for a given molecular weight, increasing charge density stretches the polymer chains through increasing electrostatic repulsion between charged units, thereby increasing the viscosity of the polymer solution.

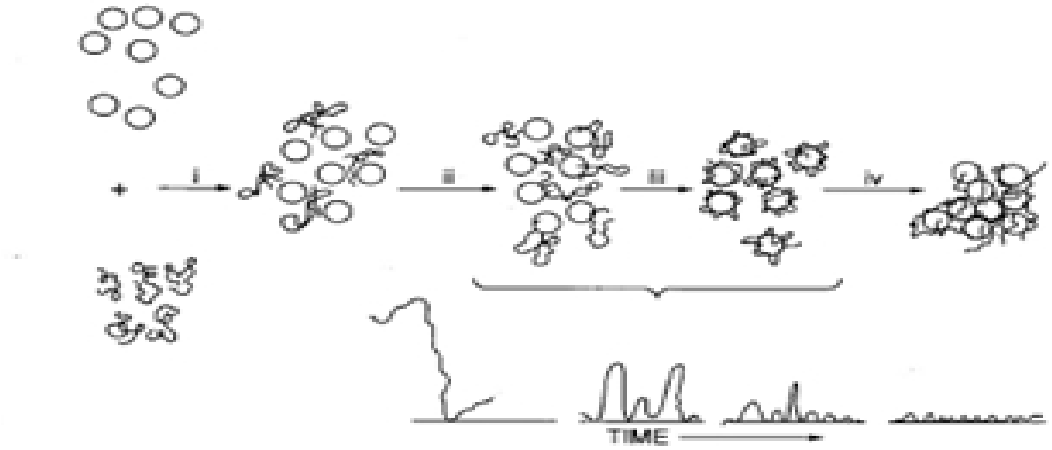


Figure 2: Stages in the bridging mechanism: (i) Dispersion; (ii) Adsorption; (iii) Compression or settling down (see inset); (iv) Collision

Equipment and reagents

- Phipps Bird Six-Place Stirrer
- Aluminum sulfate solution
- Pipettes/syringes
- Volumetric cylinders
- 0.15, 0.5, 1 and 2-liter beakers
- Turbidimeter
- Burettes
- Salt

Tasks performance order

Determine the turbidity and pH of the raw water sample.

Add 1 liter of raw water into each of the six beakers of the laboratory stirrer.

0.25%, 0.5%, 1.0%, 1.5%, 2.5% and 4.0% of 1% $Al_2(SO_4)^3$ solution were added to 6 water samples respectively. At approx. the same moment, add Alum solution into each beaker and stir at approx. 400 rpm for 1 minute. (Describe your observations in lab exercise book)

Dose of the coagulant (ml) can be calculated by the formula:

$$D = \frac{V \cdot C1}{C2},$$

Where D – dose of coagulant, ml; V – volume of water solution, ml; C1 – required concentration of coagulant, % mass; C2 – initial concentration of coagulant solution, % mass.

Decrease the speed to approx. 30 rpm and allow the sample to mix for a period of 10 minutes. Observe any changes including the flocs formation speed, appearance, size, compactness in the suspended matter in the sample.

At the end of the mixing period, turn off the stirrer and let the flocs settle for about 20 minutes. With a syringe, carefully remove the supernatant (clear liquid) from each beaker in the 150mL beaker. And determine the turbidity and pH of each of the samples.

Report content

Add all results in a Table format. (Describe your observations in lab exercise book)

Plot turbidity and pH as a function of coagulant dosage (x-axis = dosage; y-axis = turbidity or pH).

Determine the optimum dosage of coagulant based on the plot.

Coagulant			Coagulant concentration					
Raw water temperature			PH value of raw water					
Turbidity of raw water（NTU）			Volume (L)					
Experimental equipment parameters								
Beaker #		Raw	1	2	3	4	5	6
Dosage	mL							
	mg/L							
Turbidity（NTU）								
pH value of all samples								
Time of the beginning of formation flocs, min								
Time of the beginning of precipitation flocs, min								

Discussion issues

1. What is the best coagulant dosage and why?

2. Does the pH value have a significant change during the coagulation?

3. Why did the pH change with dosage? (What made them change?)

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3.2 Filtration

Lab purpose

Understand the procedures of rapid filtration and backwashing. Understand the relationship of the bed expansion and flow rates.

Theory

The water coming from the sedimentation tank are not pure and may contain some very fine suspended particles and bacteria. To remove these remaining impurities, the water is filtered through the beds of fine granular material, such as sand, anthracite coal etc. The process of passing the water through the beds of such granular materials is known as Filtration.

Rapid sand filters use relatively coarse sand and other granular media to remove particles and impurities that have been trapped in a floc through the use of flocculation chemicals - typically alum. The unfiltered water flows through the filter medium under gravity or under pumped pressure.

This filtering process is determined by two basic physical principles. First, relatively large suspended particles get stuck between the sand grains as they pass the filter medium (mechanical straining). Second, smaller particles adhere to the surface of the sand grains caused by the effect of the van der Waals forces (physical adsorption). A chemical filter-aid (i.e. coagulant or flocculant) might be added to promote additional adhesion.

During these processes more and more particles accumulate in the filter medium, increasingly causing filters clogging and decreased performance. When the filter effluent turbidity is greater than a treatment guideline, initial filtering performance can be re-achieved through backwashing by reversing the flow and causing the treated water to flow upwards through the bed. The bed is expanded and the accumulated debris and particles are separated in the surface water. Often, air is injected additionally to support the cleaning process. As soon as most particles are washed out and the backward flowing water is clear, the filter is put back to the operation.

Equipment and reagents

- Filter device
- Coagulants
- 0.02-liter volumetric cylinders
- 0.2-liter beakers Turbidmeter
- Thermometer

Tasks performance order

The filter bed was washed with wash rate of 12 - 15 L / (s·m^2) for 1 minute in order to remove the filter layer bubbles.

Measure the diameter of the filter and height of the bed. Measure the turbidity and temperature of raw water. The filtration starts with a flow rate of 8 m/h.

The turbidity of effluent is measured at 1, 3, 5, 10, 20, 30 min.

Increase the flow rate to 16 m/h, and then measure turbidity water turbidity at 1, 3, 5, 10, 20, 30 min.

Backwash with different backwashing intensity (6, 9, 12, 14, 16 L/(s·m^2). The height of the expanded bed was measured.

Report content

Table 1: Filter with different flow.

Diameter of Filter (mm)		Height of the filter bed (cm)	
Water temperature (^{O}C)		Coagulant	
Dosage of coagulant （mg/L）			
Filtration rate(m/h)	Flow(L/h)	Filtration time (min)	Turbidity of effluent (NTU)
8		0	
		1	
		3	
		5	
		10	
		20	
		30	
16		0	
		1	
		3	
		5	
		10	
		20	
		30	

Table 2: Filter expansion with different backwashing intensity and flow.

Height of the filter bed (cm)		Backwashing water temperature (^{O}C)	
Backwashing intensity (L/（s·m^2）)	Backwashing flow (L/h)	Height of expanded bed (cm)	Filter expansion rate (%)
6			
9			
12			
14			
16			

Report all results in a Tables 1 and 2.

Plot the effluent turbidity as filtration time (x-axis = filtration time; y-axis = effluent turbidity).

Plot the height of expanded bed as backwashing intensity (x-axis = backwashing intensity; y-axis = the height of expanded bed).

Discussion issues

1. What is the impact of the air bubble on the filter and backwashing performance?
2. When the turbidity of the raw water is constant, what measures can be taken to reduce the effluent turbidity of the initial filtrated water?
3. Why should backwashing intensity not be too high?

3.3 Rapid Sand Filtration and Ultrafiltration

Experiment 1**: Direct filtration of a model suspension in a rapid sand filter.**

Theory

Rapid sand filters are used in water treatment for the removal of particles from large amounts of water. The filter effectiveness depends on a number of factors that can be divided schematically in transport processes and adhesion to the filter grains. Several mechanisms are responsible for the transport of the solid particles to the surface of the filter grains. Their individual contributions depend primarily on the size of the particles which shall be retained. Experimental observations and model calculations have shown that particles on the order of 1 micrometer are most difficult to separate. For raw waters which contain a significant proportion of this fraction, it is advisable to combine the filtration with preceding coagulation/flocculation. The process is called direct filtration when the coagulant is added by flash mixing and flocculation takes place in an upstream basin or a long pipe. Under certain conditions, it may also be sufficient to dose the coagulant just before the filter inlet. Flocculation then occurs in the supernatant of the filter and in the pores of the filter bed, and the process is called flocculation filtration.

Successful removal of particles further requires that attractive surface forces become effective upon contact between the solid particles or flakes and the filter grain in order to prevent detachment of the particle by hydrodynamic forces. For an improved adhesion small amounts of organic polymers are often added to the water to be filtered. With increasing filter load the separation efficiency decreases. At the same time the flow resistance in the filter bed increases, and thus the head loss increases at constant flow. Once the solids concentration in the effluent exceeds the allowable value or the maximum head loss is reached, the filter bed must be cleaned by backwashing with air and/or water. The solids are then separated from the backwash water by sedimentation.

Rapid sand filters are usually operated downstream at a constant rate. They are often designed with two or three layers with different grain diameters in order to obtain more homogeneous distribution of the filter load and the head loss profile. In this case, coarse, light filters grains are forming the top layer and fine, heavy grains are arranged in the sublayer. The use of materials of different density is necessary to prevent the layers from mixing during backwashing.

For optimizing filter operation two aspects have to be considered: Firstly, the largest possible amount of water shall be treated during each cycle while the cleaning requirements must be met. Secondly, the backwash water demand should be kept low. For final optimization, tests at the technical scale plant are necessary. However, pilot filter experiments can be used for a comparison of removal efficiencies and head loss characteristics of different filter materials.

Tasks

A pilot filter is loaded with a kaolin suspension. The particle removal efficiency shall be examined without and with dosing of a coagulant. Furthermore, the development of the head loss profile inside the filter bed is to be observed as a function of time.

Experimental approach

The raw water tank of the pilot plant (Figure. 1) contains a suspension of 100 mg/L kaolin in tap water that is stirred continuously for homogenization. The rest of the system is filled with tap water. In the beginning of the experiment pump P1 is turned on and the flow rate is adjusted to 20 L/h at the rotameter R1. The needle valve at the effluent of the filter is adjusted in a way that the supernatant in the filter remains constant. Then the head loss profile for the unloaded filter bed is registered.

After 25 min of the test period, the dosing pump P2 is turned on, and a solution of aluminum sulfate (concentration 1 g/L Al) is dosed at a flow rate of 1 mL/min.

The following parameters are measured during the experiment:

Turbidity in the filter effluent:	continuously, with readings at every 5 minutes.
Turbidity in the feed:	after 10, 30, 60 and 90 minutes (taking samples from the recycle flow to the raw water tank).
Head loss profile:	every 30 minutes until the end of the experiment.
Total head loss:	every 10 minutes until the end of the experiment.

By controlling the rotameter R1 a constant flow rate has to be ensured. The increasing filter resistance must be compensated for by opening the needle valve in the filter effluent.

At the end of the filter run, backwashing is demonstrated. With the help of the rotameter R2 the backwash water flow rate is determined when the filter bed starts to become fluidized.

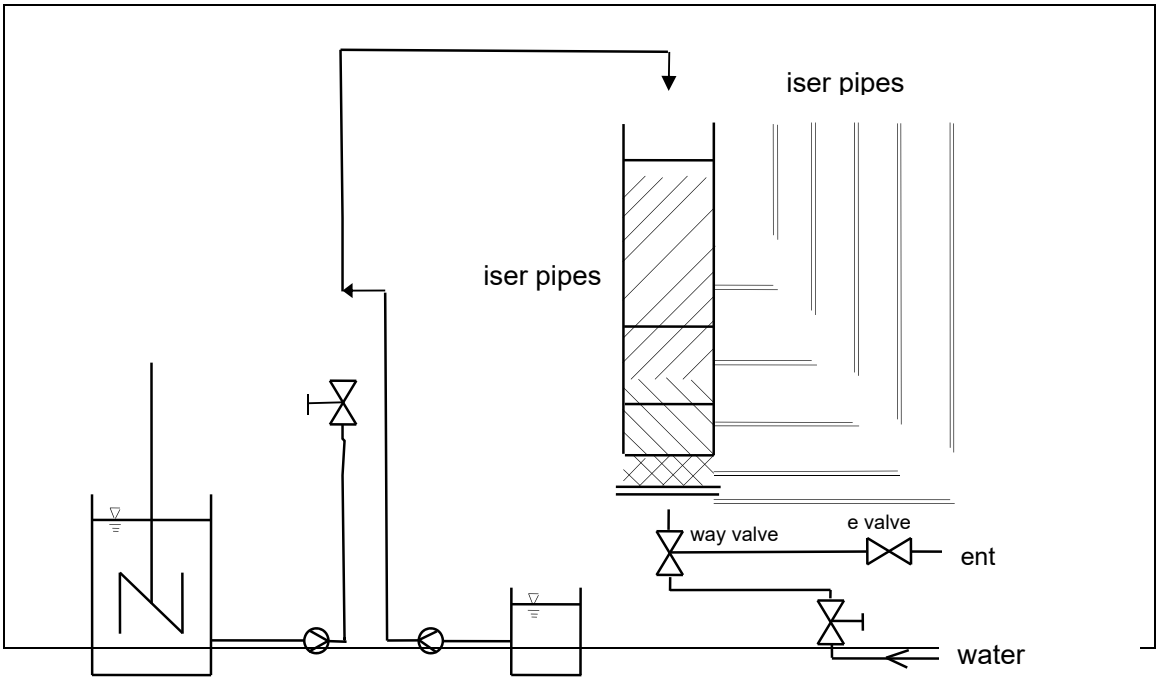


Figure 1: Sketch of the pilot filter

Discussion issues

1. What is the filter velocity and the backwash velocity, both related to the entire cross-sectional area of the filter?

2. a) The effluent turbidities shall be listed in a table and plotted as a function of time.
   b) What are the initial filter parameters obtained for the two experimental phases (without and with coagulant addition) when turbidity is used as a surrogate parameter for the concentration of kaolin?
   c) Which average filter loading σ_{kaolin} (in mL/L) is obtained at end of the test?

3. a) The head loss profiles shall be plotted as a so-called Michau-diagram.
   b) Which differences can be seen here between the two filter layers?

4 a) The total head loss shall be plotted as a function of time.
   b) What is the value of the constant b in the simplified head loss equation?

   Density of kaolin = 2.65 g/cm^3

Experiment 2**: Cross-flow ultrafiltration of a model suspension.**

Theory

Pressure driven membrane processes, including microfiltration, ultrafiltration, nanofiltration and reverse osmosis, are used not only for treating small amounts of water, but also for throughputs of >100,000 m^3/d. As a process with a cut-off in the colloidal range, ultrafiltration is used for pretreatment prior to a reverse osmosis stage, for particle removal from spring waters, and for the treatment of reservoir water. In wastewater treatment, it has become an established method for separating dispersed colloidal solids and oil droplets from suspensions or emulsions.

By concentrating the retained material on the feed side of the membrane, deposits can quickly form that will increase the head loss and change the separating properties of the membrane. Here the principle of cross-flow filtration in which the concentrate flows at high speed over the membrane, can limit these scaling and fouling effects. However, in order to come to significant yields, such systems are usually operated intermittently, that is, the concentrate is recirculated until the desired final concentration is reached. Tubular membrane bundles or rotating disks are primarily suited for this purpose.

Important design parameters are the flux, the operating pressure, and the cross-flow velocity. It is advisable to carry out tests with the water to be treated and a pilot membrane unit in order to verify these parameters. In addition, periodic membrane cleaning by flushing or back-flushing, possibly also by mechanical means, and chemical cleaning after longer time intervals must be optimized.

Ultrafiltration systems in water treatment are, however, preferably operated in the dead-end mode because of energetic reasons. Here, the retained materials must be removed from the membrane surface during short purge and backwash intervals.

Task

A model suspension of polystyrene latex beads is to be concentrated by cross-flow ultrafiltration. The flux of a capillary tube membrane shall be determined as a function of the trans-membrane pressure.

Experimental approach

A stock suspension of polystyrene latex beads (mean particle size about 0.1 microns) at a concentration of 1 g/L is given. From that, suspensions of 5 mg/L and 10 mg/L in a 0.002 molar solution of $NaHCO_3$ shall be prepared and filled in the storage tank of the test apparatus (Figure 1). At the beginning of the test, the initial turbidity of the suspension is to be determined.

Apparatus I:

The gear pump P1 is turned on and adjusted to a concentrate stream of 95 L/h with the valve at the rotameter R1 being open. At a constant setting of the pump the pressure on the concentrate side is then increased gradually by closing the rotameter valve in accordance with the following schedule:

t / min	0-5	5-10	10-15	15-20	20-25
Δp / bar	0.5	0.75	1.0	1.25	1.5

For each pressure stage, the amount of filtrate is measured using graduated cylinders and a stopwatch. At end of the test, the turbidity of the collected filtrate is measured.

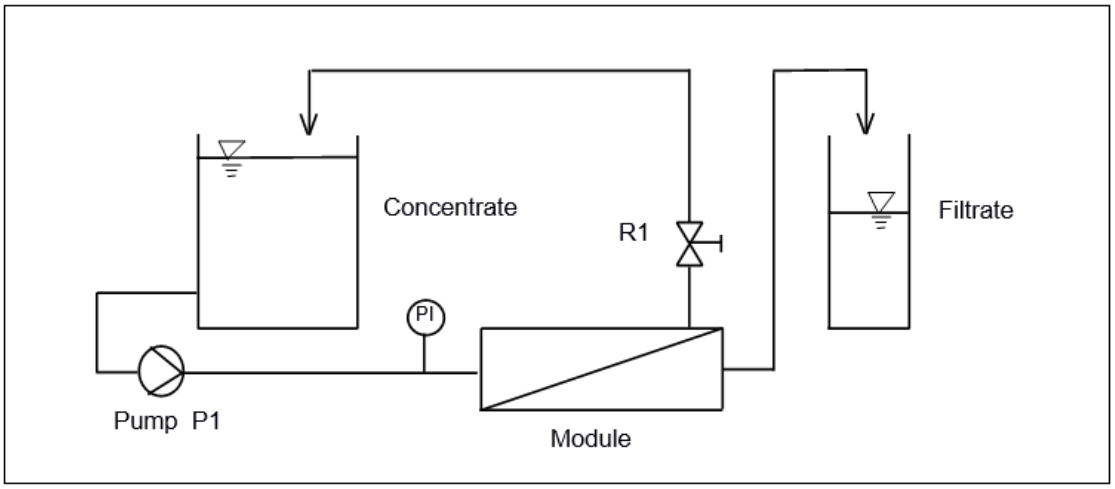


Figure 1: Sketch of Apparatus I for the investigation of cross-flow ultrafiltration.

Apparatus II:

Valve 3 is opened and valve 2 is initially kept closed. After switching on the pump, valve 2 is opened slowly while the filtrate is fed back into the storage tank. Subsequently, the setting of the excess pressure p_2 at the concentrate outflow takes place at valve 3 according to the following scheme:

Operating point	1	2	3	4	5
p_2 / bar	0.5	0.75	1.0	1.25	1.5

At each operating point, the pressure values p_1 and p_3 are read, and the amount of filtrate is determined by means of a graduated cylinder and a stopwatch. At the end of the test, the turbidity of the collected filtrate is measured.

Additional task:

100 mL samples are prepared from the colloidal stock suspension with the following concentrations: 5 mg/L; 10 mg/L; 20 mg/L; 30 mg/L and 50 mg/L. Then the respective turbidity values are measured.

Discussion issues and Evaluation

1a. The experimental data are to be listed in a table.

b. From the measured turbidities of the different colloidal suspensions a turbidity-vs-concentration calibration curve shall be derived.

From Apparatus I:

2a. The flux shall be plotted as a function of the excess pressure in the inlet.

b. What is the value of the maximum flux?

3. What is the approximate rejection of the membrane for the colloidal material?

4a. What is the value of the minimum cross-flow velocity?

b. Which maximum ratio of filtrate flow: concentrate flow has been reached?

From Apparatus II:

5a. From the pressure values p_1, p_2 and p_3, the trans-membrane pressure (TMP) shall be calculated by the following formula:

$$TMP = [(p_1 + p_2) / 2] - p_3$$

The flux shall then be plotted as a function of TMP.

b. What is the value of the maximum flux?

6. What is the approximate rejection of the membrane for the colloidal material?

Additional literature

- DVGW code of practice W 213-3 (2005), W 213-5 (2013) and W213-6 (2013)

  Filtration processes for particle removal

- Rapid sand filters
- Membrane filtration
- Control by turbidity and particle analysis

- Cheryan, M.: Ultrafiltration and Microfiltration Technomic Publ. Co., Lancaster (PA) 1998
- Melin, T., Rautenbach, R.: Membranverfahren – Grundlagen der Modul- und Anlagen-auslegung (Membrane Processes – Fundamentals of Module and Plant Design), 3. ed., Springer, Berlin 1997

3.4 Adsorption on Activated Carbon

Theory

Numerous dissolved organic substances, in particular hydrophobic species, can be efficiently removed from water by activated carbon adsorption. When describing the relevant processes, one must distinguish between the equilibrium and the kinetics of adsorption.

Adsorption equilibrium refers to the stable state which is established between the concentration of a substance in water and the surface loading of activated carbon after a sufficiently long contact time. The relationship between concentration and loading is called adsorption isotherm. It is dependent on the properties of the individual substances and on the type of activated carbon used. Isotherms cannot be predicted theoretically but must be determined experimentally. In multi-component systems, it also comes to competing effects between different substances. Earlier it was necessary to determine experimental data for the respective mixtures in order to describe multi-solute adsorption. Today, models are available that allow to predict multi-component equilibria, based on the adsorption parameters of the individual components. Most important for the adsorption capacity of an activated carbon is its large internal surface area. Therefore, the adsorption process involves the transport of molecules from the bulk solution flowing through the packed bed of activated carbon granules to the adsorption sites inside the particles.

The first transport step is the diffusion through the hydrodynamic boundary layer around the activated carbon granules. This external mass transfer, also called film diffusion, can be determined experimentally quite simply and accurately. When knowing both the diffusion characteristics of the substance, the hydrodynamic conditions and the outer surface of the activated carbon granules, the film diffusion coefficient can also be calculated from empirical mass transfer correlations.

Several mechanisms may contribute to the mass transfer inside the carbon granules. Firstly, the molecules diffuse in the pore water, on the other hand they are believed to be transported in the adsorbed state when local loading differences exist on the activated carbon surface. Parameters describing the internal mass transfer cannot be predicted but must be determined from experimental data.

Experiment 1**: Determination of a single-solute isotherm.**

Task

For the substance 4-hydroxybenzoic acid (HBA) the equilibrium loadings on activated carbon Norit ROW 0.8 S shall be determined at various residual concentrations. From the data, the parameters of the Freundlich isotherm equation are to be derived.

Experimental approach

From a stock solution of 1 g/L of HBA, test solutions with different initial concentrations according to Table 1 are prepared by dilution with distilled water. The pH value is adjusted with

HCl to pH < 3 in order to prevent pH effects on adsorption. Aliquots of 200 mL of each solution are then distributed to 5 Erlenmeyer flasks.

500 mg of finely ground activated carbon, to be stored in a desiccator, are weighed and dispersed in 0.5 L of water with the aid of a high-speed stirrer. The suspension volumes given in Tab. 1 are then withdrawn with a pipette and added to the corresponding solute samples. This type of metering is more accurate than weighing and adding dry activated carbon for amounts of activated carbon <20 mg. The flasks are sealed and continuously mixed on a shaker for at least 24 hours.

(In order to save time, the isotherms are prepared for this task one day in advance.)

Table 1: Experimental conditions for the determination of the HBA isotherm

Isotherm	HBA initial concentration (mg/L)	Dosage (mL of activated carbon suspension) Concentration of the suspension: 1 g/L				
1	10	0	2	4	8	12
2	20	0	3	6	10	15
3	30	0	4	8	12	18
4	40	0	5	10	15	20

After the mixing period, the activated carbon particles are allowed to settle for 1-2 hours. Then 20 mL of samples are taken from each flask with a syringe and filtered through 0.45 µm membrane filters. The HBA concentrations are determined photometrically at a wavelength of 255 nm. For isotherm 2, 3 and 4 it is necessary to dilute the filtrates by 1:2 (isotherm 2), 1:3 (isotherm 3) and 1:4 (isotherm 4), respectively.

Evaluation

1. The surface loading values for each isotherm point shall be calculated using the mass balance equation and listed in a table together with the residual HBA concentrations.

2. The data for all four isotherms shall be depicted in a log-log graph.

3. The parameters K_F and n of the Freundlich isotherm equation are to be determined from all data points by regression analysis using the Excel software. Outliers have to be identified and omitted here.

4. The Freundlich isotherm shall also be included in the diagram. Which measurement points show the largest deviation, and why?

Experiment 2: **Determination of the internal mass transfer coefficient.**

Task

For HBA as a model substance, diffusion inside the granules of activated carbon Norit ROW 0.8 S shall be investigated. From the experimental data, the effective internal diffusion coefficient is to be determined.

Experimental approach

In a beaker, 5 L of a HBA solution with a concentration of 10 mg/L are prepared and acidified to pH <3. Then two initial samples are taken. A representative granular activated carbon sample of about 250 mg is weighed and dispersed in distilled water in a beaker. The water is briefly heated to the boiling point in order to remove the air from the pores of activated carbon granules and cooled again. The activated carbon particles are then transferred to the screen basket of a turbine stirrer (see Figure 1).

At the beginning of the test, the stirrer is immersed into the HBA solution and set at a stirring speed of 200 min^{-1}. Then samples of 10 mL each are taken according to the following schedule:

Sample-no.	1	2	3	4	5	6	7	8
t (h)	0.25	0.5	1	2	4	6	23	25

After the test is finished, the HBA concentrations are measured photometrically in each of the samples.

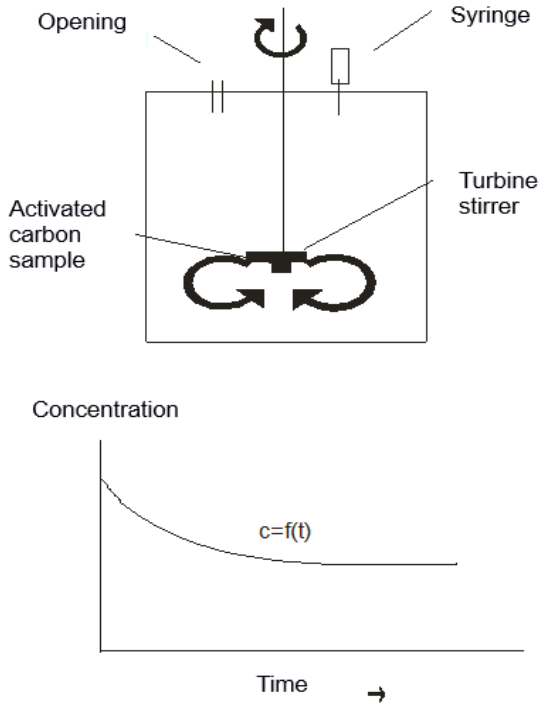


Figure 1: Apparatus for determining concentration-vs-time curves.

Evaluation

1. The measured concentrations shall be listed in a table, and the ratios of residual to initial concentration shall be plotted as a function of the square root of time.

2. The correlation of Gnielinski is to be applied to calculate the external mass transfer coefficient $ß_L$ for a superficial velocity of 100 m/h that is assumed to be an approximate value for the hydrodynamic conditions in the screen basket.

   The following parameters shall be used:

   Bed porosity $\varepsilon_F = 0.42$

   Average particle diameter $d_P = 1.18$ mm

   Kinematic viscosity (water, 20° C) $\nu = 1 * 10^{-6}$ m^2/s

   Diffusion coefficient (HBA, 20° C) $D_L = 0.77 * 10^{-9}$ m^2/s

3. The effective internal diffusion coefficient D_S shall be determined by fitting the calculated concentration-vs-time curve of the film-surface diffusion model to the measured data. (A computer program for that purpose is available in the Laboratory for Water Technology.)

Experiment 3: **Adsorption of breakthrough curves of a single-solute in a fixed-bed granular activated carbon column**

The following simulation is to be carried out in a computer pool:

1. For the adsorption of HBA in a fixed-bed of Norit ROW 0.8 S, the equilibrium parameters K_F and n, and the kinetic parameters $ß_L$ and D_S, respectively, shall be used to predict the breakthrough at different filter velocities. The operating conditions are as follows:

   Feed concentration c_0 = 10 mg/L

   Filter cross sectional area A_F = 1 m^2

   Filter bed length L = 2 m

   Bulk density of the carbon ρ_F = 374 kg/m^3

   Filter velocity v_F= 5; 10 and 15 m/h

   The mass transfer coefficient $ß_L$ = f (Re, Sc) is to be calculated for each filter velocity using the correlation of Gnielinski.
2. What is the actual residence time of the water in the filter bed?
3. When do the effluent concentrations reach 10% of the feed value, and how many bed volumes have then passed the filter?
4. Which percentage of the maximum available adsorption capacity has approximately be used in each case?

Additional literature

- DVGW code of practice W 239 (2011)

  Removing organic substances in drinking water treatment by adsorption on activated carbon.
- DVGW code of practice W 651 (M) (2013)

  Feed systems for powdered activated carbon in drinking water treatment.
- Sontheimer, H., Crittenden, J.C., Summers, S.R.

  Activated Carbon for Water Treatment. DVGW Research Center, Karlsruhe 1988

3.5 Membrane methods for cleaning water solutions: ultrafiltration, nanofiltration, reverse osmosis

Lab purpose

Studying the process of separation of water solutions by the reverse osmosis method and effect of pressure on selectivity and permeate flux.

The objects of the study are model water solutions of various salts that undergo desalination and of concentrating by the reverse osmosis method.

Theory

Membrane processes are widely used both in various technological applications and in the field of environmental protection for the purification, separation and concentration of a variety of water solutions. Also, membrane processes are used to create combined technological schemes for wastewater treatment and for the organization of closed water circulation systems.

Ultrafiltration, nanofiltration, reverse osmosis are the main membrane methods of separation of liquid systems. These methods are used to remove particles whose size is less than 1 μm.

The operating principle of a typical membrane module represents in Figure 1. The stream of feed water divided into two constituents: the first is a stream of purified water (permeate) and the second is a stream saturated with impurities (concentrate or retentate).

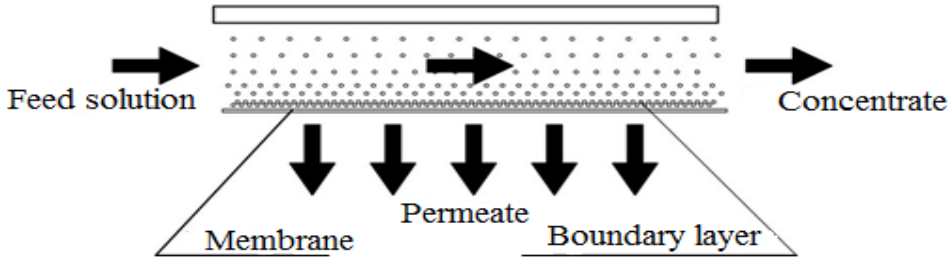


Figure 1: Schematic representation of a typical membrane module.

The main advantages of membrane methods:

• High stability of cleaning with changing parameters of the feed solution;

• Significant reduction in production areas;

• Reduction of reagent costs;

• Enough low power consumption;

• Modularity of the equipment, allowing increasing productivity easily;

• Full automation of processes;

• Possibility of economical reception of drinking water from the sea.

Ultrafiltration

Ultrafiltration is the process of membrane separation of liquid mixtures under pressure. This process based on the difference in molecular weights or the molecular dimensions of the components of the mixture that is separated. Separation occurs under the action of pressure difference on both sides of the membrane. The ultrafiltration units assemble from tubular ceramic elements, spiral elements, and hollow fibers. The pore size of the UF membranes is 0.1 to 0.01 μm.

Ultrafiltration used to separate systems in which the molecular weight of the dissolved components is much greater than the molecular weight of the solvent. Since the osmotic pressure of high molecular compounds is less than the working pressure of the liquid, ultrafiltration carried out at low pressures of 0.1 - 0.5 MPa.

Nanofiltration

Nanofiltration is the process of water admixtures separation by the membrane having a higher dense and lower-permeable selective layer than in microfiltration membranes. Accordingly, nanofiltration membranes in comparison with microfiltration membranes have higher selectivity and higher operating pressure for a given productivity. Monovalent ions (cations and anions) retained by nanofiltration membrane insignificantly, while their selectivity to multivalent ions and large ions is high. The working pressure in nanofiltration processes is usually in the range from 0.5 to 1.0 MPa.

Reverse osmosis

The reverse osmosis method consists of filtering solutions under high pressure through semipermeable membranes that pass the solvent and completely or partially retain molecules or ions of dissolved substances. If the solution and the solvent separated by a semipermeable membrane, a spontaneous transition of the solvent into the solution takes place. This phenomenon called osmosis (Figure 2a). The pressure at which equilibrium sets in (Figure 2b) called osmotic pressure, When high pressure is applied at the side of the solution that is greater than the osmotic pressure, the transfer of the solvent will be carried out in the reverse direction (reverse osmosis), and the dissolved substance is retained partially or completely (Fig. 2c).

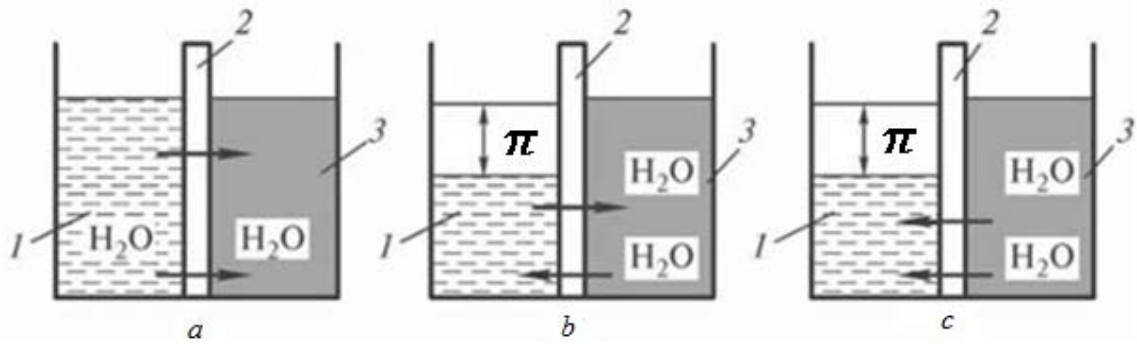


Figure 2 - The scheme of occurrence of reverse osmosis: a - direct osmosis, P <π; b - osmotic equilibrium, P = π; c - reverse osmosis, P> π; 1 - pure water; 2-membrane; 3 -water solution

The pressure π in the solution, which causes the passage of the solvent through the membrane, is called the osmotic pressure. The value of the osmotic pressure for solutions is determined by the Van't Hoff equation:

$$\pi = \frac{i \cdot R \cdot T \cdot C}{M} \quad (3.4.1)$$

i - the isotonic coefficient; T - the absolute temperature of the solution, K; R - the universal gas constant (8,310 J/mol · K); C - the concentration of dissolved salt (g/m^3); M - the molecular weight of the salt (g/mol).

The isotonic coefficient is calculated by the formula:

$$i = 1 + \alpha(n - 1) \quad (3.4.2)$$

α - the dissociation degree of the dissolved salt; n - the number of ions that are formed upon the dissociation of the dissolved salt.

The higher the concentration of the solution to be purified, the higher the osmotic pressure drop and the greater the hydrodynamic pressure required to realize the water purification.

Osmotic pressure of solutions can reach tens of megapascals (MPa). The operating pressure for reverse osmosis should be significantly greater because the productivity determined by the driving force of the process which is the difference between working pressure and osmotic pressure. The operating pressure in reverse osmosis processes is usually in the range of 1.0 to 10.0 MPa. For example, at an osmotic pressure of 2.45 MPa for seawater, which contains 3.6% of salts, the operating pressure in desalination plants should be maintained at 6.85-7.85 MPa.

The methods of ultrafiltration, nanofiltration and reverse osmosis have much in common, in particular, in the field of apparatus design, but there are enough differences (Table 1.).

Table 1: Comparison of ultrafiltration, nanofiltration and reverse osmosis.

Process	Ultrafiltration	Nanofiltration	Reverse osmosis
Pore size, μm	0,1 -0,001	0,01 -0,001	0,001 -0,0001
Operating pressure, MPa	0,1-0,5	0,5-1,0	1,0-10,0
Separation	Macromolecules, proteins, polysaccharides, viruses	High-molecular organic substances, multivalent ions	Low-, high-molecular organic substances, ions, molecules
Energy consumption	Low (0,1 -0,2 kWh / m^3)	Moderately low (0,2 -0,9 kWh / m^3)	Moderate (0,9 -3,7 kWh / m^3)

The main parameters that characterize the process of membrane separation of liquid solutions are selectivity (φ) and permeate flux (G). Selectivity - the ability of the membrane to have different permeability for different components of the mixture to be separated.

The selectivity of the separation process using semipermeable membranes is determined by the formula:

$$\varphi = \frac{C_{fs} - C_p}{C_{fs}} \cdot 100 = (1 - \frac{C_p}{C_{fs}}) \cdot 100 \text{ , \%,} \quad (3.4.3)$$

where: C_{fs} and C_p - the concentration of the feed solution and permeate, respectively.

Permeate flux of the membrane is the amount of matter passing through the unit surface of the membrane per unit time. Permeate flux of the membrane calculated by the formula:

$$G = \frac{V}{F \cdot \tau}, \text{ m}^3/\text{m}^2\text{s}, \quad (3.4.4)$$

where: V - the volume of permeate, m^3; F - working area of the membrane, m^2; τ - the time, s.

The permeate flux and degree of cleaning affected by several parameters, namely: applied pressure; temperature; yield of permeate; concentration of salts in the source water.

Membrane plant - a set of devices and technical equipment that provides the process of membrane separation. The membrane installation includes two main elements:

1. Device for creating fluid pressure (pump);

2. A membrane apparatus that provides the necessary membrane surface.

These elements are basic in the installation scheme for the membrane separation process (Figure 3).

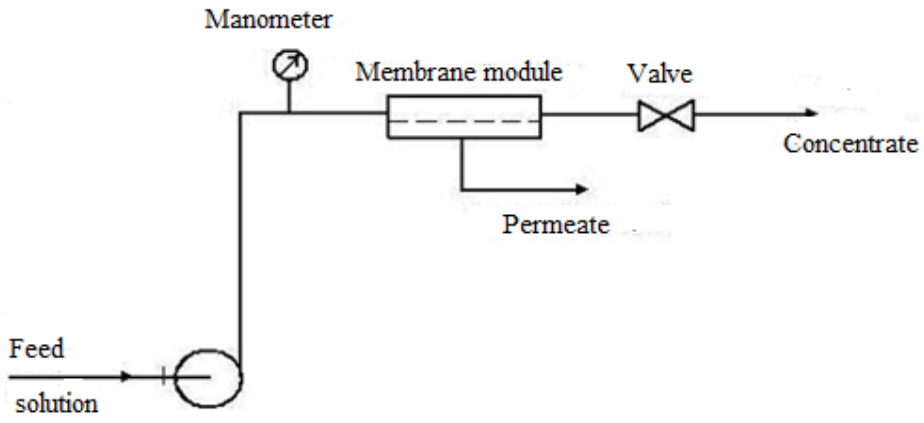


Figure 3: The scheme of installation for the membrane separation process [1].

Membrane apparatus is a device for performing a process of membrane separation of the feed solution into a filtrate (permeate) and a concentrate (retanate), which includes structural elements for introducing the feed water and for removing permeate and concentrate.

Membrane apparatus should have a high packing density - the surface of semipermeable membranes per unit volume of the apparatus, be easy to assemble and operate. When processing solutions and colloidal systems, it is necessary to create conditions for their uniform distribution to reduce the effect of concentration polarization. According to the method of packing membranes, apparatuses divided into four main types:

- with flat sheet membrane elements;
- with tubular membrane elements;
- with membrane elements of the spiral type;
- with membranes in the form of hollow fibers.

All these devices usually assembled from separate, so-called, membrane elements, the design of which characterizes this apparatus.

Equipment and reagents

- Installation of reverse osmosis "Ecosoft 2500 MO-F3A" with a module of storage tanks.
- Glasses for sampling.
- Laboratory conductometer MP 521, ULAB (Conductometer MP 521, ULAB)
- Reagents for preparation of model solutions.

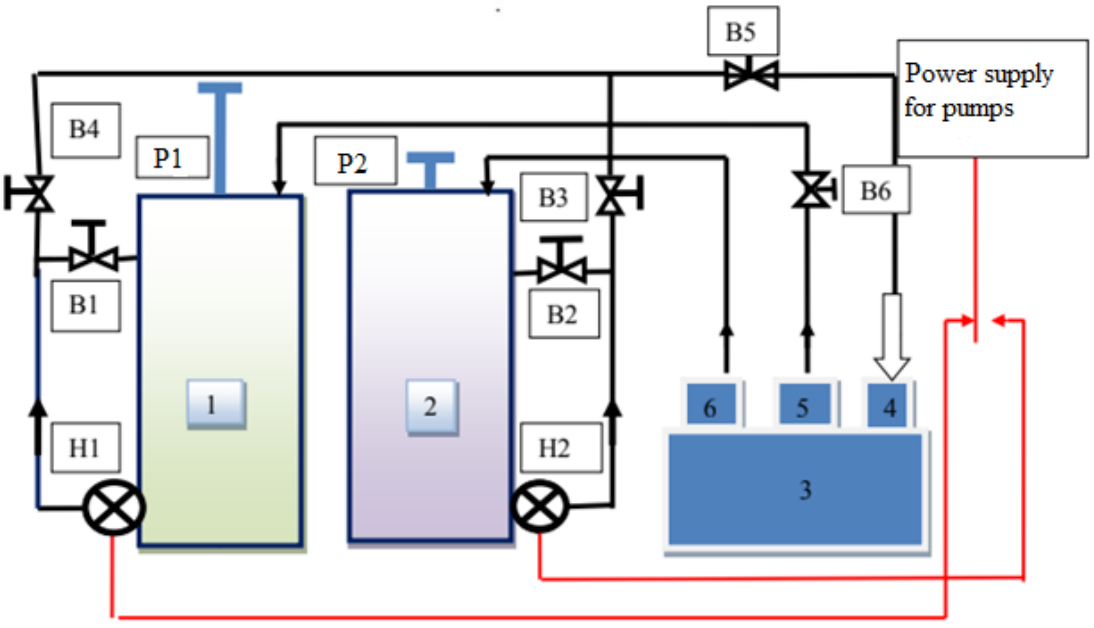


Figure 4: The scheme of the experimental setup [2]: 1 - tank for the feed solution and accumulation of permeate; 2 - tank for accumulation of concentrate; 3 - installation of reverse osmosis "Ecosoft 2500 ME-F3A"; 4 - input of the feed solution for treatment; 5 – permeate output; 6 - concentrate output; H1, H2 - centrifugal pumps; B1-B6 - ball valves; P1, P2 - float level gauges.

Tasks performance order

- Prepare a model solution by dissolving the salt in water (the type of salt and its concentration in the model solution is set by the teacher). The volume of the solution must be at least 80 dm^3.
- Install the reverse osmosis "EcoSoft 2500 MO-F3A" in accordance with the instructions. Set the initial working pressure level Prab = 0.4 MPa on the manometer.
- After three minutes of operation at a given operating pressure, take samples of permeate and concentrate for analysis.
- Using a laboratory conductometer, in accordance with the instructions attached to this instrument, determine the salt content of the feed solution (S_{fs}), permeate (C_p) and concentrate (C_c) in ppm (mg / dm^3) and write the data in Table 2.
- According to the indications of rotameters, determine the permeate (I_p) and concentrate (I_c) consumption in dm^3 / min. Write the data in Table 2. Calculate the flow rate of the feed solution using the formula:

  $$I_{fs} = I_p + I_c,$$

  Write the result to the table 1.
- Repeat the operations on items 3-6, setting the working pressure level $P_{working}$ = 0.5; 0.6; 0.7 and 0.8 MPa and write the results in Table 2.
- Calculate the membrane selectivity by the formula (3), the permeate flux (G) according to the formula (4) and record the data in Table 3.

Report content

Table 2: The results of an experimental investigation of salt solution.

$P_{working}$, (MPa)	I_p, dm^3/min	C_p, mg/dm^3	I_c, dm^3/min	C_c , mg/dm^3	I_{fs}, dm^3/min	C_{fs}, mg/dm^3
0.4						
0.5						
0.6						
0.7						
0.8						

Table 3: The results of calculation of membrane parameters.

$P_{working}$, (MPa)	0.4	0.5	0.6	0.7	0.8
φ,%					
G, $m^3/m^2 \cdot s$					

Discussion issues

Using the data in Table 2:

1. Plot the curve of function of permeate flow and salt concentration in permeate upon working pressure I_p = f (Pworking) and C_p = f (Pworking).

2. Plot the curve of function of concentrate consumption and concentration of salt in the concentrate on the working pressure Ic = f (Pworking) and C_c = f (Pworking).

3. Plot the graph of the flow rate of the feed solution on the operating pressure I_{fs} = f (Pworking).

Using the data in Table 3:

1. Plot the graph dependences of selectivity and permeate flux on the working pressure φ = f (Pworking) and G = f (Pworking).

2. Describe the shape of the obtained curves and formulate the conclusions.

3. Explain how results obtained results are consistent with theory.

4. To explain how it is possible to reduce the amount of waste that is generated during the purification of salt solutions by the reverse osmosis method.

References

1. Physico-chemical methods of water purification. Management of water resources. Edited by I.M. Astrelin and H.Ratanavira. Project “Water Harmony”, Private limited company “Drukarnya Volf”., 2015. - 578 p.
2. Methodical instructions to the laboratory practice course on the theoretical basis of chemistry and water technology / Contributors: VS Gevod, N.G. Borisova - Dnipropetrovsk: DNVZ UDKhTU, 2016. - 68 p.

4 Operation

4.1 Microscopy of activated sludge

Microscopy

Biodegradable substances are the main compound of the organic load in domestic wastewater. These substances are working as

In municipal wastewater, degradable organic substances make up a large part of the burden. These substances have a nutrient function for heterotrophic microorganisms and are degraded by microorganisms in water bodies into which wastewater is discharged. Existing species grow and new species can be established according to the nutrient supply. Since this biodegradation of organic substances is associated with a consumption of respiratory oxygen, this "self - purification of the water bodies" is limited.

Because of the increase in sewerage since the industrial revolution (from around 1850), especially in densely populated areas, technical wastewater treatment became necessary. For example, sewage treatment plants have been in operation since around 1900, and biological sewage treatment plants have been increasing since about 1950, exploiting the degradation activity of microorganisms.

Normally the wastewater in a wastewater treatment plant flows first through a screen for the removal of coarse material, then through a grit trap in which mineral particles settle and then into a primary clarifier in which solids are deposited. Substances with a higher density sink to the bottom, substances that are lighter than water accumulates on the surface.

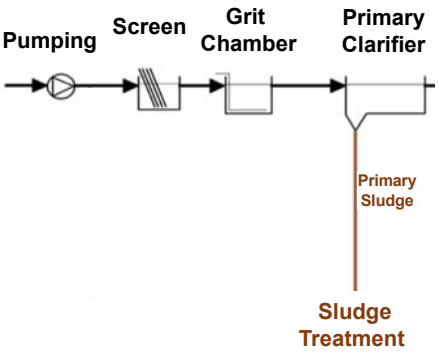


Figure 1: Flow scheme of a mechanical wastewater treatment.

After this mechanical treatment, the wastewater still contains dissolved organic substances and on a low-level organic particles as well, which are degraded in the following biological stage.

Here are mostly activated sludge basins (or trickling filters) in use. In activated sludge basins, colony-forming bacteria and organic and inorganic wastewater substances form activated sludge flocs that are barely visible to the naked eye.

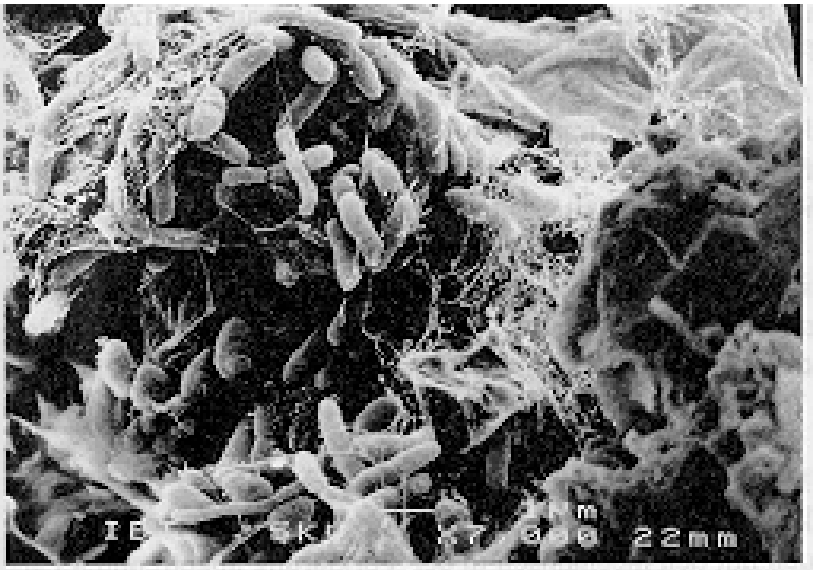


Figure 2: Electron microscopic figure of an activated sludge floc (8 mm equals to 1 µm;).

Only at high magnifications, individual bacteria forming a colony are visible in the flocs. The bacteria excrete a gelatinous matrix (EPS, extracellular polymeric substances) in which they remain embedded, even after cell division; fine filaments, which are visible only in the electron microscope, link the individual cells. (The actual activated sludge floc then also includes inclusions and mounting, mostly unicellular, organisms.)

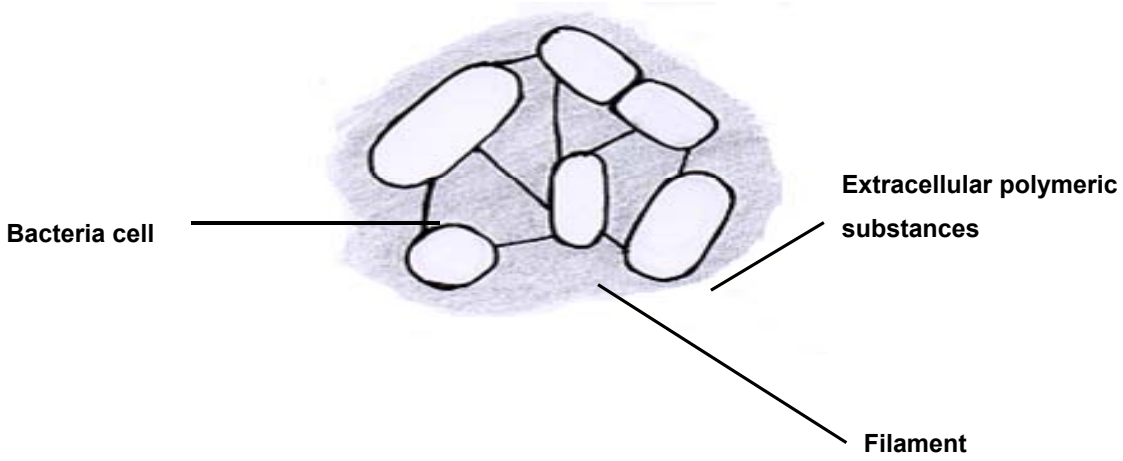


Figure 3: Section across a colony of bacteria.

Bacteria required for wastewater treatment are found in the wastewater itself or they establish themselves in wastewater and in wastewater treatment plants due to abiotic factors that are suitable for them; only their number is insufficient. Thus, biological purification processes were able to prevail only when it was possible to increase the biomass in activated sludge by a sludge recycling at the beginning of the 20th century. This kind of wastewater treatment is the most common way of purifying wastewater.

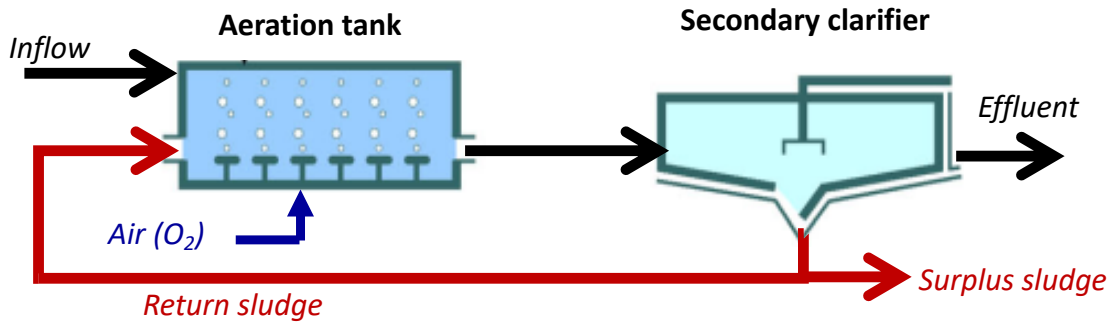


Figure 3: Biological wastewater treatment with the return of sedimentation sludge into the aeration tank

The shape of the activated sludge flocs and the kind of species, as well as the individual density of the growing community of organisms (biocenosis), are dependent on many abiotic factors such as temperature, oxygen concentration, pH, nutrient composition and concentration, the presence of possible pollutants and hydraulics. Biotic factors such as feeding behaviour, predator - prey relationships or parasitism also influence the morphology of the flocs.

Thus, from the microscopic picture and its potential changes, valuable conclusions can be drawn on wastewater composition and operating conditions. By regularly examining the activated sludge of a treatment plant (for example 2 to 3 times a week) and recording the observed details, changes can be detected that go beyond normal and constant fluctuations. Early reactions before manifesting disturbances are possible.

For a reliable assessment of the state of a wastewater treatment plant, the microscopic image should never be used alone, moreover the combination of physical measurements and chemical and biological determinations are useful.

Practice of microscoping

The microscope

1. Binocular tube
2. Connector with oculars
3. Turret for objects
4. Achromate objectives
5. Object leader
6. Sockets for objet
7. Driving buttons for displacement of objects in x- and y-direction
8. Knurled screw for fixing of the obects
9. Object table
10. Condensor
11. Additional lense
12. Aperture diaphragm
13. Slider with diffusing screen
14. Lightning socket with filter
15. Coarse and fine adjustment

Figure 4: Microscope and its units.

By using a phase contrast device, delicate structures such as e.g. flagellums become more visible; they appear black against a gray background. For the determination of many activated sludge organisms, a phase contrast is mandatory. To do this, you must insert a suitable loose slide into the slot provided for each objective (10x or 40x) in the condenser. When changing the lens, do not forget to change the slider!

The preparations

Aqueous preparations are examined directly and alive. For this purpose, a not too large drop of the sludge is placed on an object carrier (for example with a glass rod or pipette) and carefully covered with a cover glass. The cover glass is not allowed not "float" (deglaze excess liquid with paper). It is not allowed to push the cover glass over the sample; The flocs are otherwise transformed into "sausages" and can no longer be judged.

The investigation

The activated sludge sample is examined using the microscopy form (next pages). As a rule, the preparation and consideration of several preparations are necessary to complete the form for a sludge sample. There are several reasons for this: examining multiple grab samples from the sampling container allows a better overview of the content: organisms may burst or change due to lack of oxygen (under the coverslip!). By this a correct determination becomes impossible. The worst case the preparations can dry out.

The evaluation of the microscopic image is in accordance with the microscopy form.

First, a species list (tax list) is created qualitatively on the microscopy form. Here, the order of the organisms should correspond to the system. Then the levels of frequency are estimated.

For frequency levels, the attributes "rare" for a single find and "plentiful" for such a high density of the organism that there is hardly any room for other species. are assigned. Remaining levels are distributed between these attributes. In case of doubt, the trophic position of the species should be considered. To classify e.g. predatory species, which are at the top of the food pyramid and thus exert a relatively high pressure on the entire ecosystem, tend to be slightly higher. Bacterial or detritus eaters, which are the basis of the food pyramid, are classified rather lower.

Generally, the findings are compiled on the microscopy form and show a consistent picture of the operating state of the wastewater treatment plant. In actual WWTP investigations, physical, chemical, hydraulic and other biological parameters are included in the overall interpretation.

----------Microscopic Investigation----------

WWTP: Date:

Place of sampling:

1. Morphology of the sludge flocs

Size	small (<150µm)	medium (150 - 500µm)	large (>500µm)
Shape	rounded	irregular	elongated
Structure	compact	irregular	fluffy
Edge	sharp (smooth)	mid-sharp	diffuse (rugged)

2. Bacteria (estimated frequency)

					
	rare	multiple	frequent	very frequent	plentiful
free bacteria					
filamentous bacteria					

3. Mono and multi-cellular organism

					
	rare	multiple	frequent	very frequent	plentiful

Assessment of the flocs

Four different parameters describe the morphology of activated sludge flocs: size, shape, structure and edge.

First, the size is estimated: small flocs have a diameter below 150 µm, medium flocs between 150 and 500 µm and large flocs have a diameter of about 500 µm. As an aid for the estimation, an exact length measurement serves us at the beginning, which we can perform in a microscope with the eyepiece micrometer integrated there.

The size of the flocs has an effect on their settling behavior in the secondary clarifier. Very small flocs are too light to sediment and leave the sewage treatment plant with the treated wastewater. Such "pin-point" flocs may e.g. caused by heavy metal poisoning or by excessive shear forces. Very large flocs have too little metabolically active surface relatively. Flocs of medium size are desirable, possibly weighted by attached animal organisms.

The shape of activated sludge flocs is often irregular. Rounded shapes indicate high sludge age, elongated shapes may be a hint for industrial wastewater. Round flocs sediment better than elongated ones.

With regard to their structure, flocs of a sludge can have compact as well as loose areas; their percentage can be stated in%. Often floc edges are loosely structured and the fluff centers are compact. These areas usually contain older bacterial material; they appear brown or dark brown in the microscope and are often rounded. Loose, visually bright and delicately translucent areas are formed by young, newly grown bacterial colonies or foothills of these colonies; they are metabolically active.

The assessment of the sharpness of the floc edge is essential, as it allows direct conclusions about the sludge age via the growth activity of colony-forming bacteria.

Rounded, compact, dark flocs usually have a smooth, sharp edge. They consist of older, less metabolically active organisms (high sludge age). Fissured, fuzzy floc margins consist of young, rapidly growing bacterial colonies, which can be recognized in the phase contrast at a 400-fold magnification in a regular punctuation: these are the individual bacterial cells. Such fluffy structured, blurred floc edges indicate a low sludge age and thus a high metabolic activity.

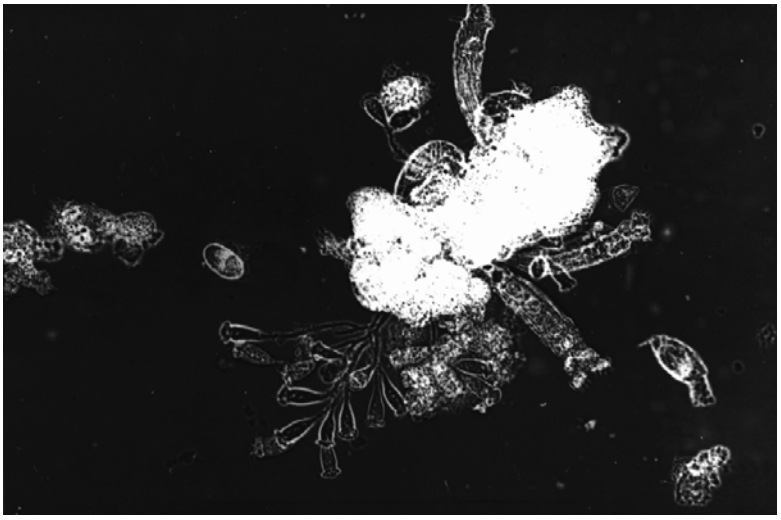


Figure 5: Bacteria floc with a high sludge age.

Figure 5 shows a medium-sized activated sludge floc that has a rounded shape and a compact structure. This sludge has a good sedimentation behavior. The edge of the floc is sharp; you could easily draw the outline of the floc with a pen in one go. This sharp edge indicates a high sludge age. This is confirmed by the monocellular and multicellular organisms that occur on and beside the floc.

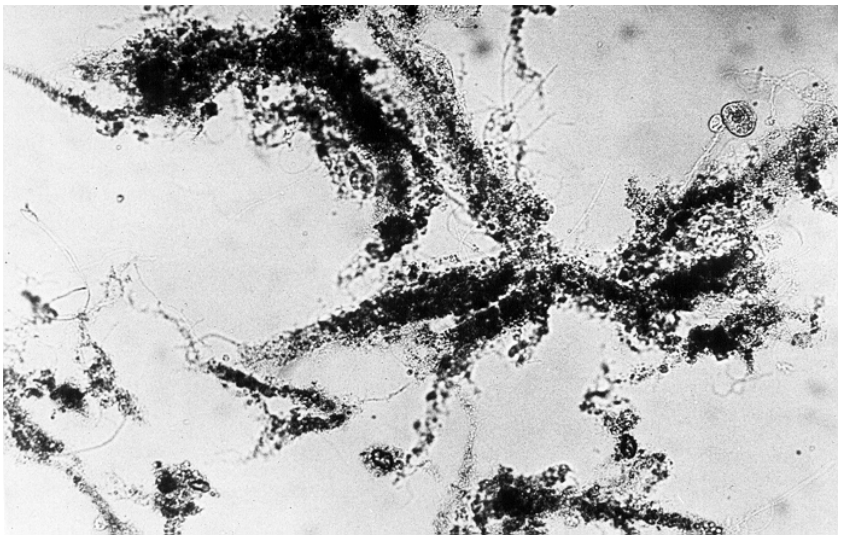


Figure 6: Bacteria floc with a low sludge age.

The activated sludge flocs in Figure 6 are also medium in size but have an elongated shape and an irregular structure. Compact areas, especially towards the edge of the flocs, turn into fluffy areas. The edge itself is diffuse. This fuzziness or outgrowth of the flocs towards the edge is caused by the growth of young bacterial colonies, whose individual cells are so clearly visible only in sludges with a low sludge age. In this example, load sizes and hydraulic parameters were used to calculate a sludge age of only 2 days. The sedimentation behavior is not as good as with the first sludge (SV = 180 ml / l).

Bacteria

The individual densities of all organisms are recorded in a semi-**quantitative** method. Their frequency is estimated on a five-point scale, and the terms "rare, multiple, frequent, very frequent, or mass" are given.

The qualitative detection of the organisms takes place on different levels. Monocellular and multicellular animal organisms, as well as the few occurring plant organisms, are determined on the basis of morphological characteristics - if possible up to the species - with specific literature. In bacteria, this approach is not possible; they are morphologically too similar. In order to determine bacterial genera or species very costly floral analyses must be carried out. The result that could be achieved would not justify the high cost of routine activated sludge testing. For normal controls of wastewater treatment plants, it is sufficient to assign the bacteria occurring to some functional groups that can be identified morphologically by light microscopy (Figure 7).

Mono or cell structure	Description	Examination for wastewater treatment
Single free bacteria 	Mostly mobile, predominantly cocci or sticks, many species, e.g. from the generic group Bacillus, Pseudomonas; (1 - 3 µm)	Causing turbid effluent, negative
Spirochaetes 	Very mobile, fine spirally wound filaments often buckled	-
Colonies of bacteria 	Recognized by the regular puncturing, often at floc edges, numerous species, e.g. Zoogloea ramigera	Floc forming, positive
Filamenteous bacteria 	Filamentous cell aggregates, individual cells often not recognizable, some species branched. Typical representatives: Spaerotilus natans, type 021 N, Nocardia sp.	Dominant behavior worsens sedimentation behavior, negative
Spirilla 	Very large (e.g., 10 µm long), rigid body, spirally wound, fast-floating, microaerophilic, e.g. Spirillum volutans (PHB granules as reserve substance), Thiospira sp. (Sulfur bacterium)	indicator for lack of oxygen, negative
Sulphur bacteria 	to SO_4^{2-}, in H_2S oversupply elemental S is incorporated into cells, highly refractive, e.g. Beggiatoa alba, Thiothrix nivea, Thiospira sp.	indicator for lack of oxygen and in addition indicator for aus H_2S negative

Figure 7: Functional groups of bacteria in activated sludge systems

In the form "Microscopic investigation" single bacteria and filamentous bacteria are listed separately and must be estimated separately in their frequency because of their importance for the treatment plant operation.

Free bacteria are understood as round, rod-shaped, curved or spiral (spirochaetes) single cells. They appear black in the phase contrast setting of the microscope against a light background. They are detached from any flock dressings and burden the wastewater treatment process. They can be mobile or immobile.

Bacterial colonies are often fast-growing bacteria that blur the edge of a flake. They are then recognized by a regular puncture, the individual fresh, young cells. They often belong to the generic group "Zoogloea sp." and are also referred as "tree bacteria". In the activated sludge form, they are detected by the characterization of the edge of the floc.

The frequency determination of **filamentous bacteria** is of major importance in the case of the sludge bulking problem. At least one preparation must be completely screened at 100x magnification. The respective frequency level is compared with internationally uniformly used photos; This is to ensure a comparability of all findings worldwide (EIKELBOOM & VAN BUIJSEN, 1987). There is one photograph each for the filament categories 0 and 1 (rare and

multiple) used in the filamentous bacteria (Figure 8). For the categories 2, 3 and 4 (frequently, very frequently and in large numbers), there are two photos each (Figure 9 to Figure 11), with thinner or thicker filamentous bacterial species.

Activated sludges with a high proportion of filamentous species among the bacteria have a poor sedimentation behavior. The sludge may under certain circumstances not be adequately thickened and does not reach the dry matter contents necessary for a satisfactory cleaning. In the case of hydraulic turbulences, e.g. due to stormwater, a large part of the biomass can be lost with the effluent of the sewage treatment plant.

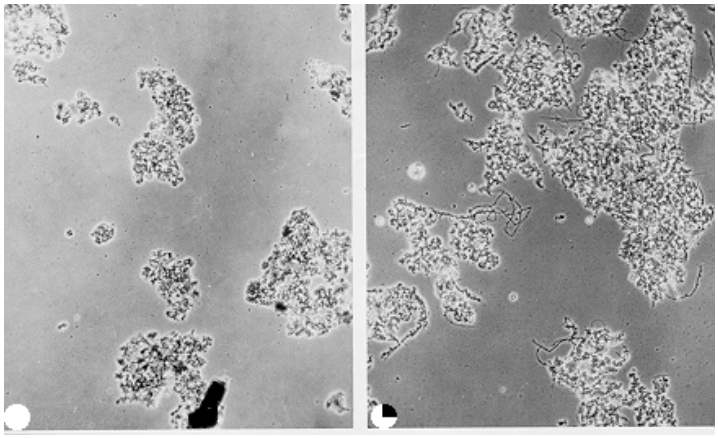


Figure 8: Activated sludge of the filament category 0 (rare) (left) and category 1 (multiple) (right)

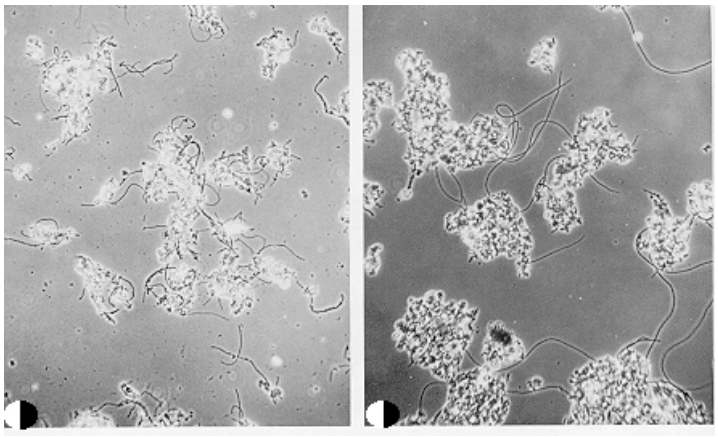


Figure 9: Activated sludge of the filament category 2 (frequent) - left side: sludge with multiple thick filaments right side: sludge with a few thick filaments

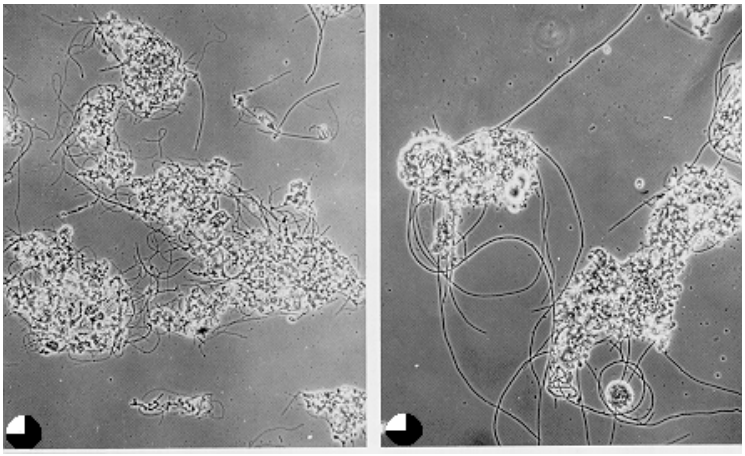


Figure 10: Activated sludge of the filament category 3 (very frequent) - left side: sludge with multiple thin filaments right side: sludge with multiple thin filaments

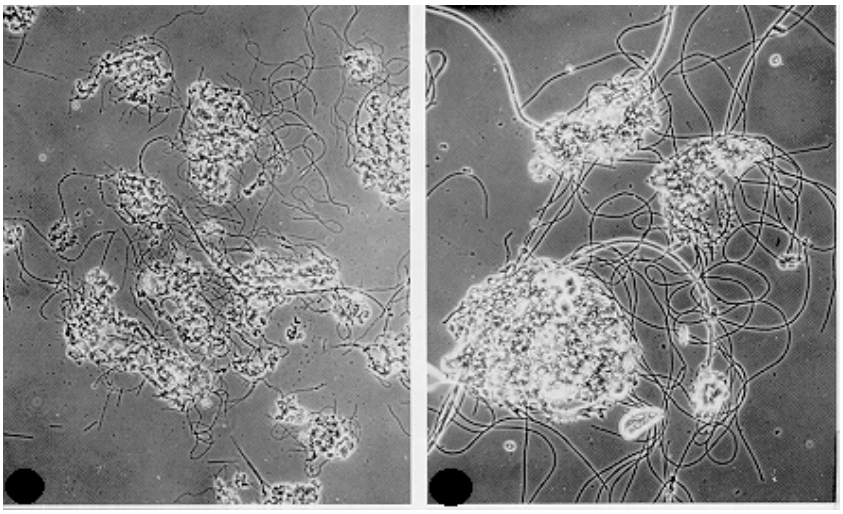


Figure 11: Activated sludge of the filament category 4 (plentiful) - left side: sludge with plenty of thin filaments right side: sludge with plenty thick filaments

A significant group of bacteria in activated sludge are spirillas; they are in the shape of a short, rigid spiral (unlike spirochaetes). They are important indicators of a lack of oxygen. Some of them belong to the group of sulphur bacteria, which can also be filamentous. Sulphur bacteria are ever indicators for hydrogen sulfide (H_2S).

Organism			Size	Food	Generation time	Movement	Indicator for
Plants		green algae	3-100 µm	c-autotroph	h	prn. flagellum	light
		Funghis	10-50 µm wide	c-heterotroph	h	no	low pH
Animals	unicellular organism	Flagellates	5-70 µm 10-20 µm	bacteria or particular and dissolved organic matter	h	flagella	high load (imbalance)
		Amoebae	10-200 µm 30-100 µm	bacteria or particular and dissolved organic matter	h	Pseudopodia	high load (industry)
		Ciliates	15-2000 µm 30-200 µm	bacteria, algae, detritus, flagellates, Ccliates	h/d	clia/cirri	depending on species different water qualities
		Suctories	50 µm - 1 mm	Flagellaten, Ciliaten	d	no	high sludge age, low toxicity
	multicellular organism	Rotifers	50 µm - 3 mm	filter feeder, bacteria, detritus, small preys	d	with rotifer organ and foot, fixed on surfaces	high sludge age
		Gastrotrichs	0.4 - 1,5 mm	organic particles, small preys	d	creeping, winding, floating	high sludge age
		Nematodes	0,2 - 5 mm	detritus, small preys, algae	d	winding (turgor)	high sludge age
		Annelids	1 - 20 mm	detritus bacteria	d	creeping (bristles)	high sludge age
		Tardigrades	50 µm - 1.2 mm	plants, nematodes, rotifers	d	running (3 pairs of leg)	high sludge age
		Miltes	1 - 4 mm	predatory	d/weeks	creeping, 4 pairs of legs	high sludge age
		Crustacea	1 - 5 mm	Phytoplankton	d	floating	low load
		Insects, Psychoda	larva: 4 mm Imago: 3mm	larva: biofilm	weeks	Larva: creeping Imago: flying	biofilm in trickling filters

Figure 12: Organisms in activated sludge and biofilms in trickling filters

Vegetable Organism

An overview of organisms occurring in activated sludge systems and biofilms in trickling filters is given in Figure 12.

Plants are relatively rare in activated sludge systems. Green algae, which use light for photosynthesis, are not specifically used for wastewater treatment in our latitudes. Nevertheless, biofilms grow on the upper areas of tanks edges, where green algae have a high

proportion. These can be detached and found randomly in the microscopic picture. In biofilms of open trickling filters, green algae can grow in quantities and make up a large part of the biofilm.

Funghi hyphae are more frequent than algae in activated sludge systems. They contribute to the degradation of organic compounds with their heterotrophic metabolism. Preferentially they grow at low pH-values and - similar to filamentous bacteria - can cause a bad sedimentation of the activated sludge. The difference to filamentous bacteria is there 10 times higher width.

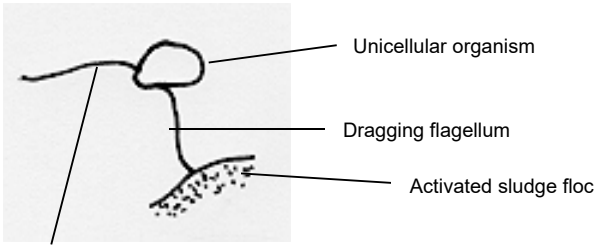
Animal unicellular organism

Flagellates

Usually, Flagellates occur in a normal activated sludge with several species. On the one hand, they are food competitors for bacteria by uptaking dissolved organic substances, on the other hand, they eat organic particles, for example bacteria cells. They themselves are often eaten by ciliates. Flagellates are frequent in highly loaded sludge. Most species swim very fast with the help of one or more flagella, which can sometimes be seen in the microscope, even in phase contrast, only after prolonged observation.

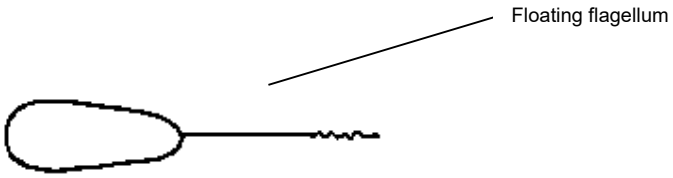
Four frequent types are known:

1. Fitted with floating and dragging flagellum



Pleuromonas jaculans

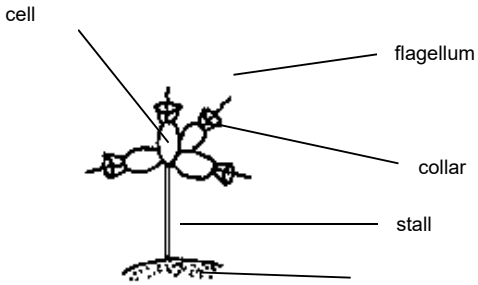
2. Fitted with floating flagellum stretched forward



Peranema sp.

To the generic group Peranema belong very large (40 - 70 μm) flagellates, which swim slowly. They are metabolites, that means, they can change their shape.

3. Fitted with collar and flagellum



Codosiga sp.

Flagellates with collar and flagellum my occur solitarily (like demonstrated in the sketch) or as a colony. In comparison to the two species described before they are more rare.

4. fitted with multiple symmetrical arranged flagella

Trepomonas agilis

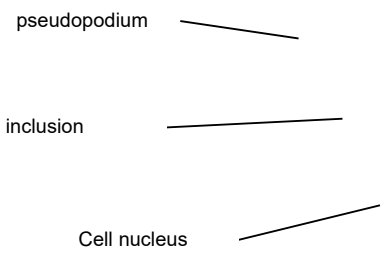
The generic group Trepomonas is easily recognizable by its staggering swimming motion. The species are indicators of a lack of oxygen.

Amoebae

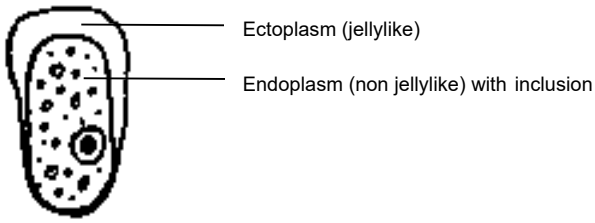
Amoebae occur in the soil, in the water and as parasites. In balanced activated sludge systems, they are almost always found in low numbers of individuals. They are often found in heavily loaded sludge systems or in sludge systems that are not in equilibrium. They move very slowly, if at all, and are often overlooked by inexperienced eyes.

Two morphological groups of amoebae are easy to distinguish:

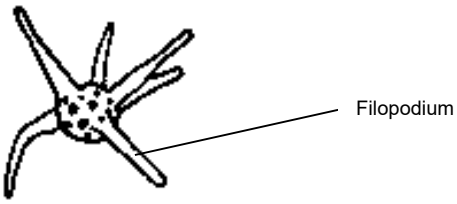
1. Naked amoebae, which evert fake feet out of their body plasma and are using this for movement of taking up their food.



Chaos sp.

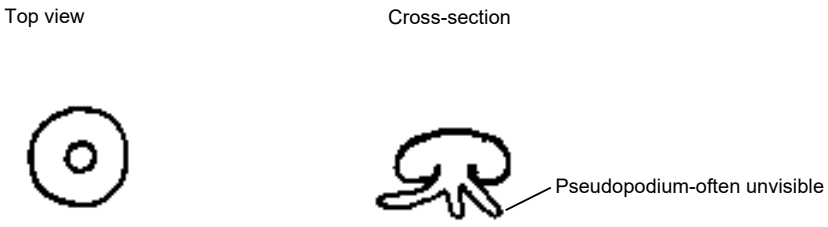


Vahlkampfia sp.

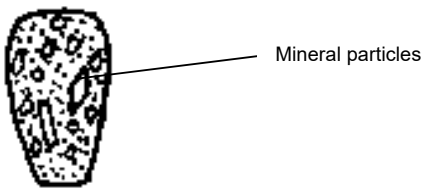


Astramoeba sp.

2. Shell amoebae, which excrete a shel produces from body's own organic substance. In this shell foreign objects (grains of sand, diatom shells) can be incorporated or reinforced with silica plates. An opening, from which the fake feet can reach out, is located in the shell.



Arcella sp.



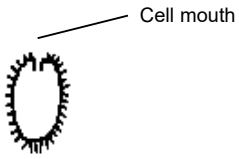
Difflugia sp.

Ciliates

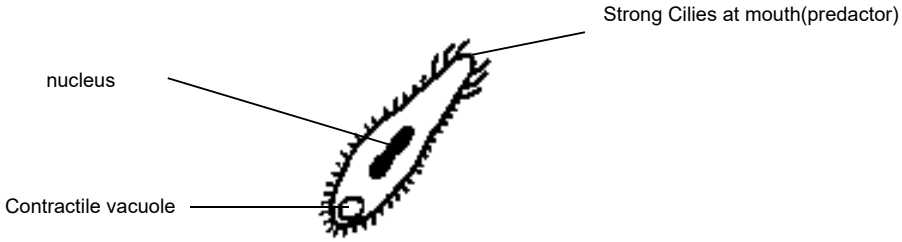
Ciliates are very sophisticated and highly differentiated protozoa. Many types have mouth and anus, they have a precursor of a nervous system and muscle fibers, their eyelashes are similar to them in human bodies. Ciliates have a simple excretory system for dietary fibers. Furthermore, they have the possibility of the exchange of genetic material between partners, which serves as a genetic refresher and they possess a mechanical and chemical defense systems, which is used to ward off enemies. Approximately 7,500 species are known so far. Of these, about 20 to 30 species occur in activated sludge systems. Many species are good indicator organisms for various abiotic factors; thus, ciliates are an essential group of organisms for characterizing the operating conditions in bioreactors or for the determination of the flow water quality.

Three systematic groups can be identified:

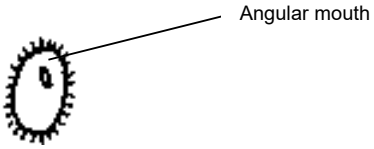
1. Holotriche ciliates, which are eyelashed entirely:



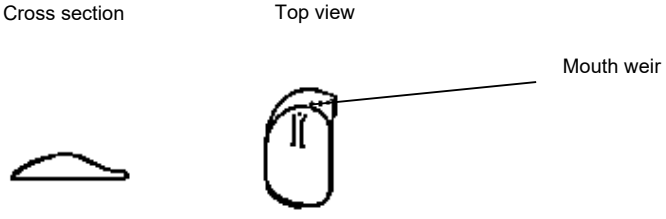
Prorodon sp.



Trachelophyllum pusillum

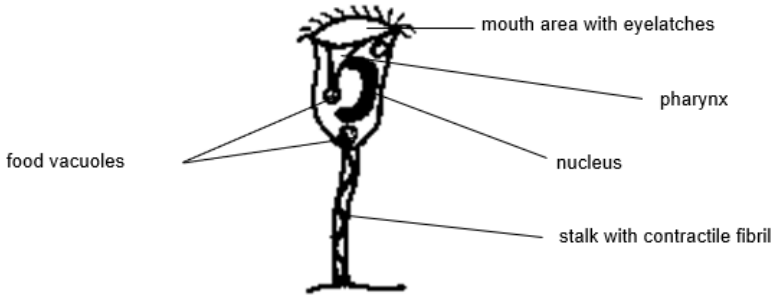


Glaucoma sp.

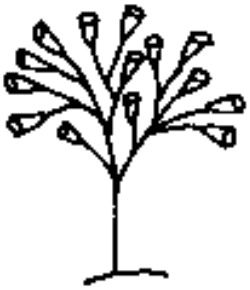


Chilodonella sp.

2. Peritriche ciliates, sessile "vorticellas" whose eyelates is reduced to wreaths around the mouth.

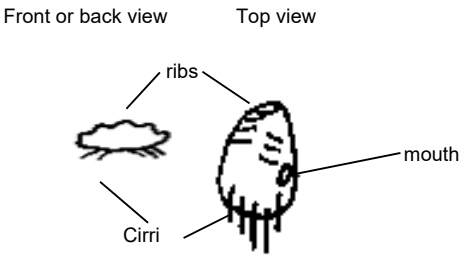


Vorticella convallaria

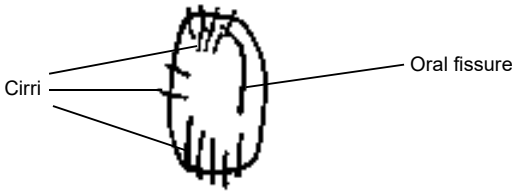


Epistylis sp.

3. Spirotriche ciliates, which eyelatches transmuted to legs - similar to motion organels. These legs are used for running over activated sludge flocs



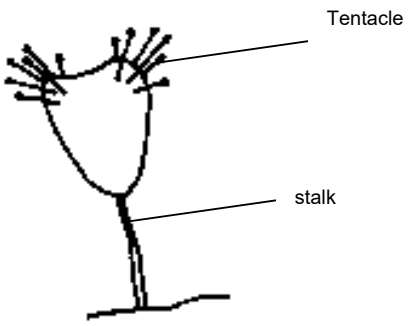
Aspidisca costata



Euplotes sp.

Suktorians

Suktorians are welcome organisms in activated sludge. They are indicator organisms for a high sludge age and all species are predatorily and are on top of the food pyramid. In addition, they are very sensitive to toxic impacts.



Tocophrya sp.

Multicellular organism

All multicellular organism are indicators of a high sludge age.

Rotifers feed by filtration; they are frequently found in harmonic activated sludge. They eat individual free bacteria and thus cause desired clear processes from the sewage treatment plant.

Gastrotrichs are closely related to the rotifers, but their occurrence is rare.

Nematodes are also known from the soil or as parasites. In activated sludge they occur occasionally only.

Annelids can become abundant in over-aged activated sludge and then eat enormous amounts of activated sludge due to their size, so that their mass and thus their age decrease rapidly. A nitrification can thus come to a standstill and the degradation can be reduced.

Tardigrades are organisms of uncertain systematic status; they probably regressed from the group of insects.

Mites can occur in over-aged activated sludge.

Crustaceans and **insect larvae** can occur in secondary sedimentation basins and in biofilms of trickling filter.

Additional microscopic examinations

In addition to a microscopic examination of activated sludge, further microscopic examinations can provide additional information on the entire treatment plant operation or can be used specifically for disturbances in the search for causes.

Figure 13 shows useful sampling points.

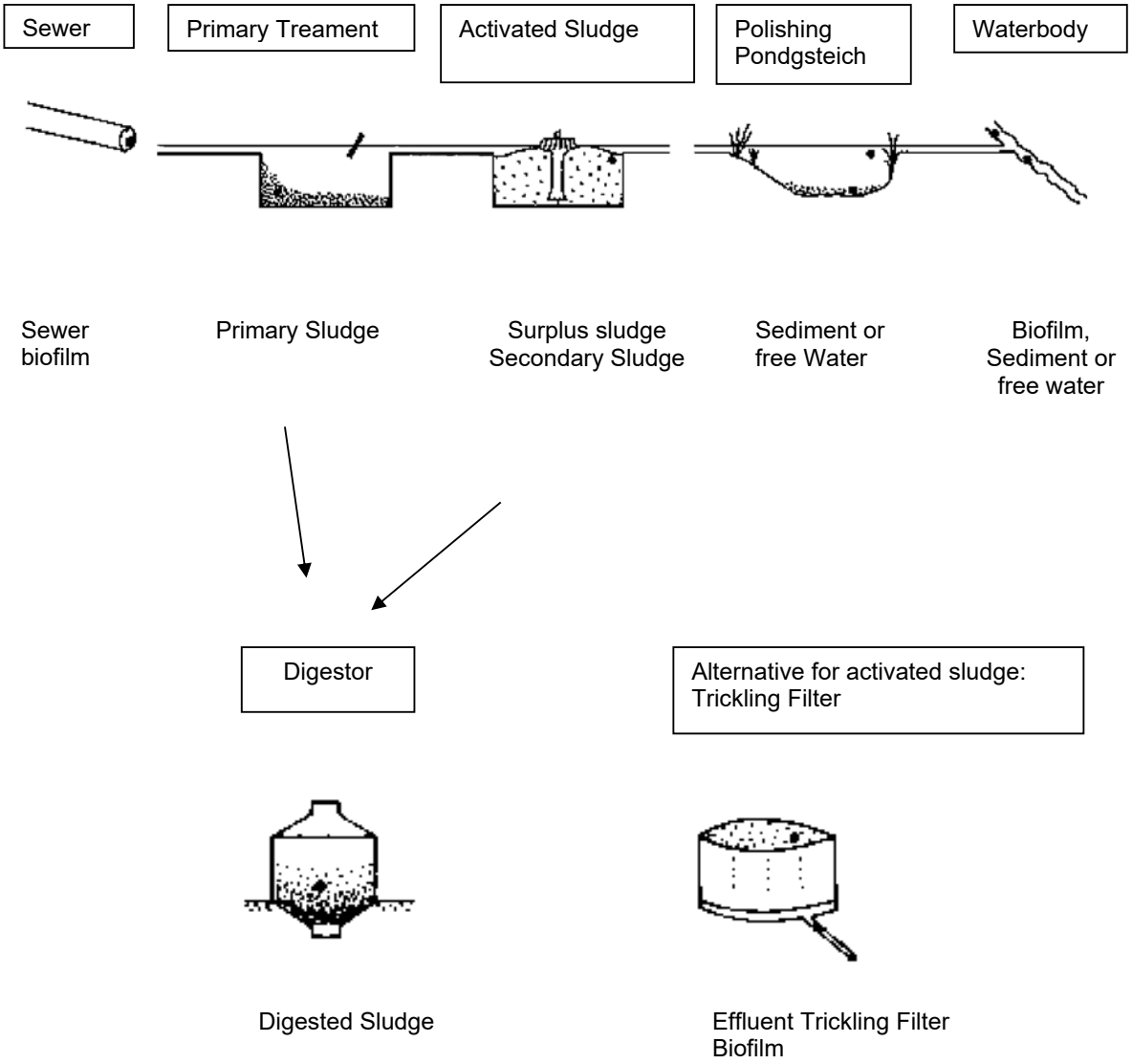


Figure 13: Potential sampling points for samples used for microscopical investigations.

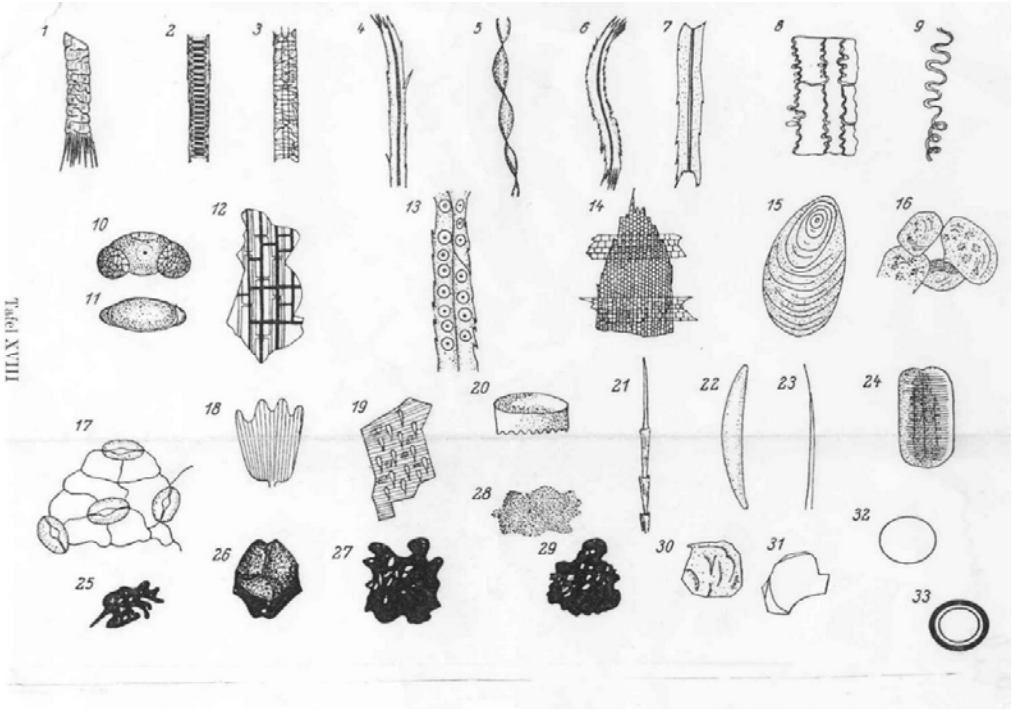


Figure 14: Unhabited sinking and floating matter in water (Liebmann, 1962)

1 wool fiber
2 rat hair
3 human hair
4 hemp fiber
5 cotton fiber
6 and 7 paper fiber
8 epidermis rest of a grass leaf
9 spiral fiber of plant tissue
10 pine pollen, fresh
11 pine pollen, dead
12 stems or root remnants
13 softwood fibers
14 softwood residue
15 starch grain from the potato
16 potato cells
17 leaf underside with stomata
18 butterfly scales
19 chitin residue
20 Body ring of an insect
21 Down stream of a feather
22 sponge needle
23 worm bristles
24 meat muscle fiber (undigested)
25 soot particles
26 hard coal
27 brown coal
28 iron oxide hydrate
29 sulfuric iron
30 grain of sand
31 pieces of glass
32 oil drops
33 air bubble

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2. Berger, Foissner, Kohlmann (1997): Bestimmung und Ökologie der Mikrosaprobien nach DIN 38410; Gustav Fischer Verlag, Stuttgart (in German)
3. Eikelboom, D.H., Van Buijsen, H.J.J. (1992): Handbuch für die mikroskopische Schlammuntersuchung; 3. Aufl. Hirthammer, München (in German)
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4.2 Optimizing recovery of RO under different salinity

Lab purpose

The goal of this laboratory work is to study a practical approach for optimizing the operation of RO systems, maximizing permeate flow, salt rejection and recovery while minimizing operating and maintenance costs, that means minimizing operating pressure and membrane fouling.

Theory

Initially designed for seawater desalination, reverse osmosis (RO) is widely applied in water treatment today: from small-scale systems under kitchen sinks in households to large plants producing water for cities, meeting new challenges to conserve water, control environmental pollution and reclaim both water and valued resources.

Due to recent advances in membrane science, modern RO membranes offer high rejection rates at reasonably high permeability together with good fouling resistance, reduced energy consumption and operational costs. Reverse osmosis systems are operated today as single-standing units or in combination with other processes like ion exchange, electro-deionization etc.

This laboratory guideline is designed as the test protocol that provides scale-up data such as permeate flux and permeate quality as a function of feed pressure and system recovery. The test method consists of determining the desalinating ability and permeate flow rate of the reverse osmosis unit. It is useful for simulation of water treatment efficiency and suited for both general environmental engineering courses as well as special courses on mass transfer, separation processes or unit operations.

Typically, reverse osmosis covers the wide range of applications by raw water salinity – from 50 mg/L and up to 50 000 mg/L. Basically, RO is a pressure-driven membrane separation process, the driving force resulting from the difference of the electro-chemical potential on both sides of the membrane. Molecular separation size for RO is below 200 Da, therefore it retains salts to a high extent.

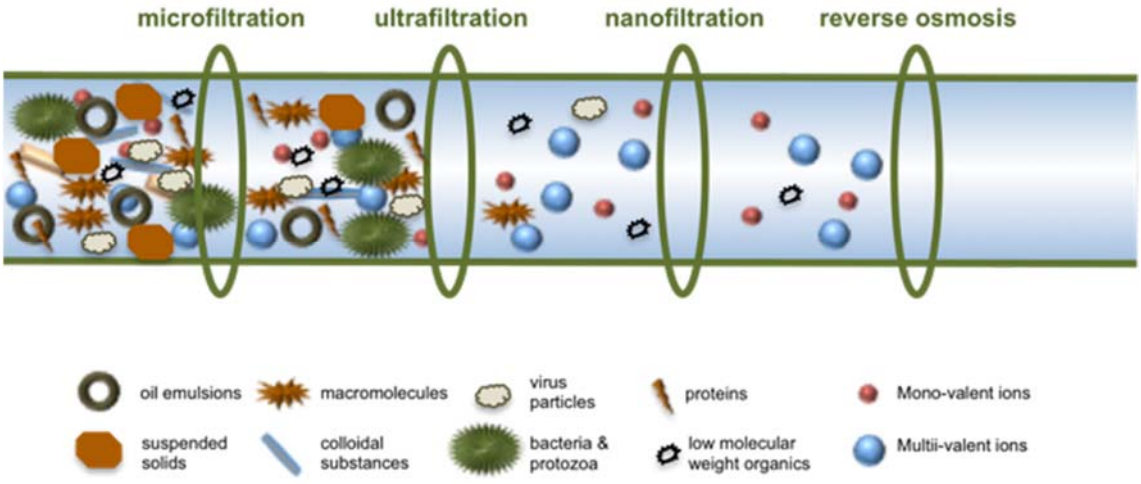


Figure 1: Membrane processes spectrum [1]

In comparison with conventional porous membranes (Microfiltration and Ultrafiltration), RO membranes are dense. Separation by pore membranes (MF, UF) is based on a sieving effect, while differences in solubility and diffusivity are responsible for the selectivity of solution-diffusion membranes (NF, RO) [2]. Asymmetric polymer or composite membranes are used

today providing rejection of dissolved salts typically at 95% to greater than 99%, depending on polymer type, feed composition, temperature and unit design.

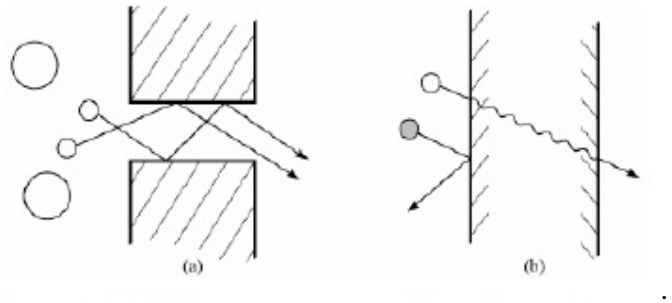


Figure 2: Mass transport through membranes: (a) pore-flow and (b) solution-diffusion [3]

The simplified solution-diffusion model describes performance of RO membrane in terms of permeate flow (under constant feed pressure) and salt rejection or salt passage:

$$Q_i = A_i \overline{\pi}_i S_E (\mathrm{TCF})(\mathrm{FF})\left(P_{fi} - \frac{\Delta P_{fc\,i}}{2} - P_{pi} - \overline{\pi} + \pi_{pi}\right) \quad (1)$$

$$C_{p_j} = B(C_{fc\,j})(pf_i)(\mathrm{TCF})\frac{S_E}{Q_i} \quad (2)$$

where: A is the membrane permeability coefficient
B is the membrane rejection coefficient
pi – average concentrate/permeate side osmotic pressure
S – wetted surface area
TCF – temperature correction factor
FF – fouling factor
P – pressure

The membrane selectivity or salt rejection is dependent on several factors and increases with the decrease of:

- degree of dissociation: less dissociated compounds are better rejected
- ionic charge: polyvalent ions are better rejected than monovalent ions
- molecular weight
- non-polarity: less polar substances are rejected better
- degree of hydration: higher hydrated ion are better rejected

RO membranes are typically operated in the cross-flow mode in the pressure range 5-70 bar and up to 120 bar in special cases. In the cross-flow mode the feed water is pumped “parallel” (tangentially) to the membrane surface, and the permeate is withdrawn diagonally to it. This is the principal difference from the dead-end operation similar to coffee filter.

The main advantage of the cross-flow is that the formation of cake layer on the membrane surface is diminished because there is a continuous turbulent flow over the membrane. This can be done with membrane modules of spiral-wound, tube, plate, cushion or disc-tube type.

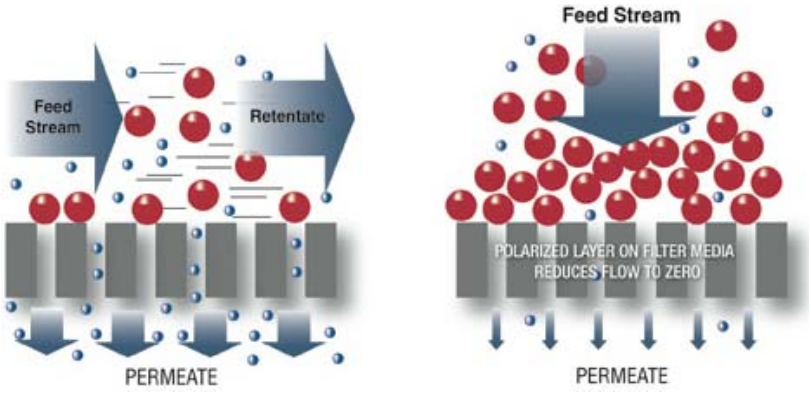


Figure 3: Cross-flow and dead-end filtration [4]

The most widely applied RO module type in water treatment is spiral-wound. It consists of several membrane bags that are wound helically with one spacer each around the permeate collecting tube and spacers inside the bags, allowing permeate to flow between the membranes. The bags are glued at three sides and attached to the perforated permeate collection pipe at the open side. The cylindrical module resulting from the whirl is supplied to the front with the feed, which flows through the module in an axial direction. While the feed flows through the space outside of the membrane bags resulting from the feed spacer, the withdrawn permeate flows in the membrane bags helically to the permeate collection pipe [5].

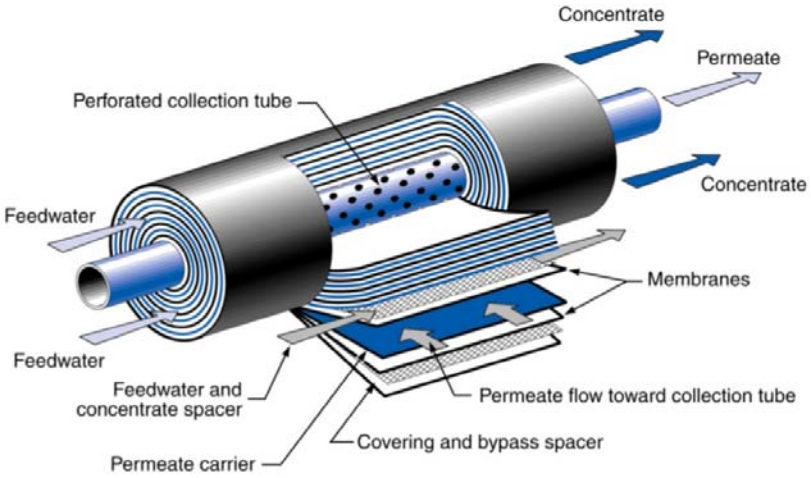


Figure 4: Spiral-wound membrane element [6]

Several membrane elements can be connected in series or in parallel and arranged in a membrane stage this way, together with necessary pumps, valves etc.

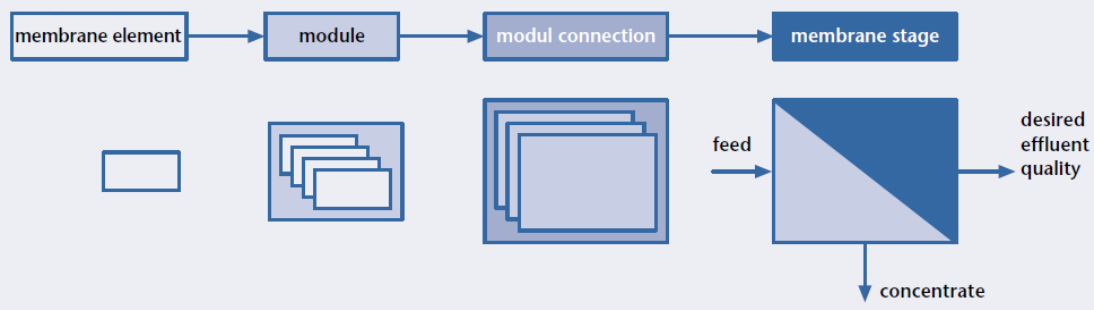


Figure 5: From membrane element to membrane stage [5]

The key terms used in reverse osmosis are:

- Permeate – purified product water produced by RO unit
- Concentrate – flow of concentrated salts from the RO unit
- Membrane flux – the rate of permeate transported per unit of membrane area in liters per square meter per hour (L/m^2h)
- Recovery – the percentage of feed converted to permeate, typically maximized while preventing precipitation within membrane system
- Salt rejection – the percentage of solute concentration removed from the feed by the membrane
- Salt passage – opposite to rejection

Flux and rejection are the key performance parameters of RO and under specific conditions are intrinsic properties of the membrane, influenced by pressure, temperature, recovery and feed water salinity.

From a practical point of view, the task of optimization of RO system operation is to **maximize** permeate flow, salt rejection and recovery, while **minimizing** operating and maintenance costs, that means minimizing operating pressure and membrane fouling.

Typically, RO unit performance is characterized by two parameters: permeate flow and quality referenced to a given feed water composition, operating pressure and recovery. The goal of RO system adjustment is to minimize operating pressure, while maximizing permeate quality and recovery at required permeate flow. The feed pressure needed to produce the required permeate flow for a given membrane depends on the designed permeate flux that has to be limited to minimize fouling. A system designed with high permeate flux rates is likely to experience higher fouling rates and more frequent chemical cleaning.

In typical single-module system, the feed water from the high-pressure pump flows to the feed inlet, the permeate stream leaves the system at no more than 0.3 bar over atmospheric pressure and the concentrate leaves the module at essentially the feed pressure, but with account of 0.3-2 bar pressure drop from feed inlet. The concentrate flowrate is controlled by the concentrate valve and should not exceed the designed value. To achieve this, while increasing the system recovery to more than 50%, concentrate recycling is organized. A part of the concentrate goes to drain, while the other part is recycled and added to the suction side. A high fraction of the concentrate being recycled helps reducing element recovery, while keeping the system recovery reasonably high.

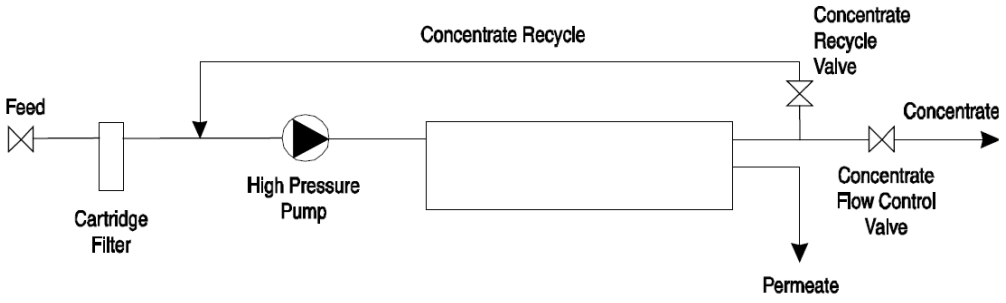


Figure 6: Typical single-module system [7]

Equipment, materials and methods

Recommended RO units are Ecosoft MO6000 or MO10000 (provided to the partners through the Water Harmony projects), but any other similar unit is suitable.

Portable or laboratory TDS-meter or conductivity meter

Portable or laboratory pH-meter

The RO unit diagram and the principle of its operation is illustrated here:

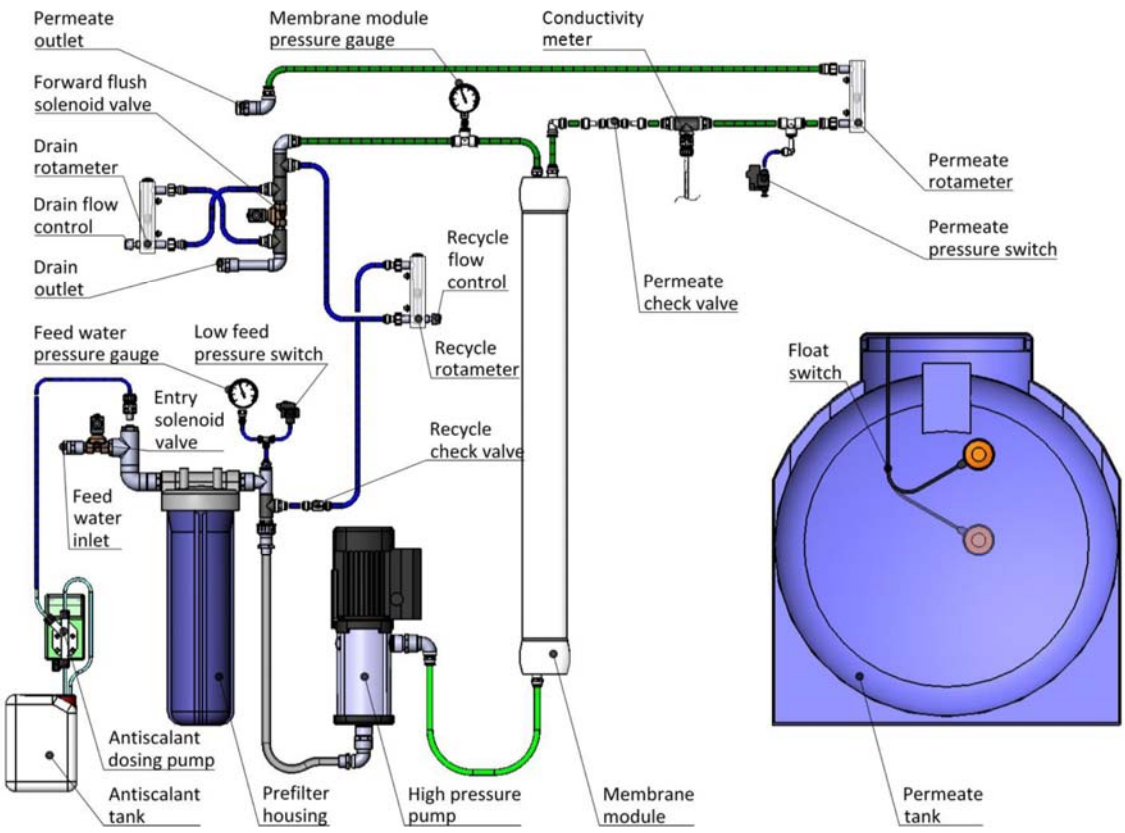
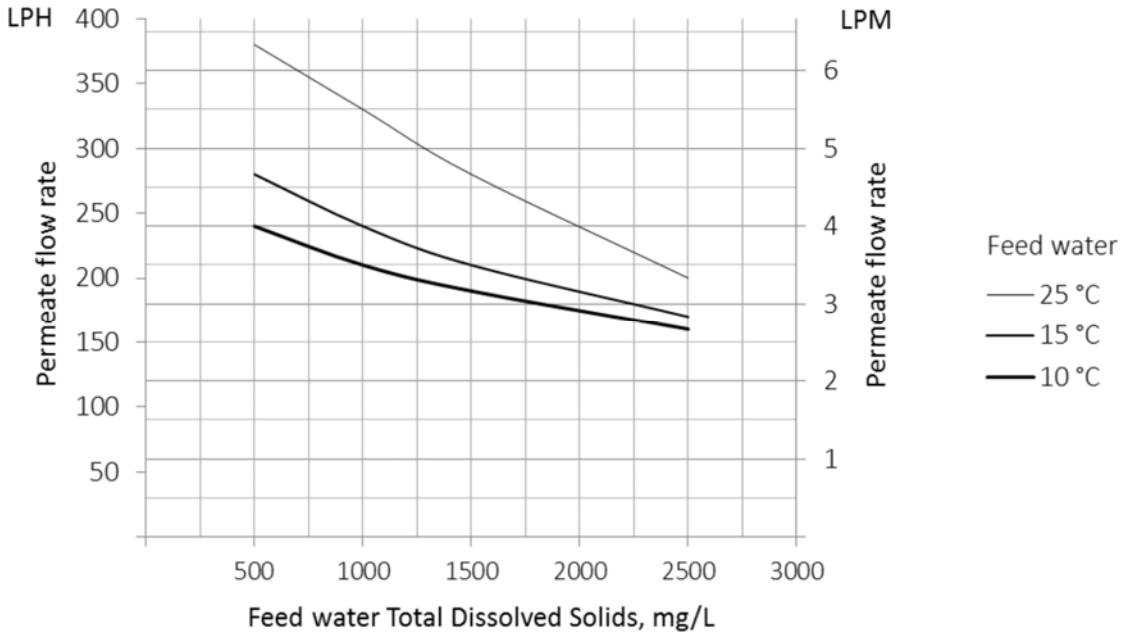


Figure 7: RO unit diagram (unit of 10 m^3/d capacity is equipped with two membranes) [8]

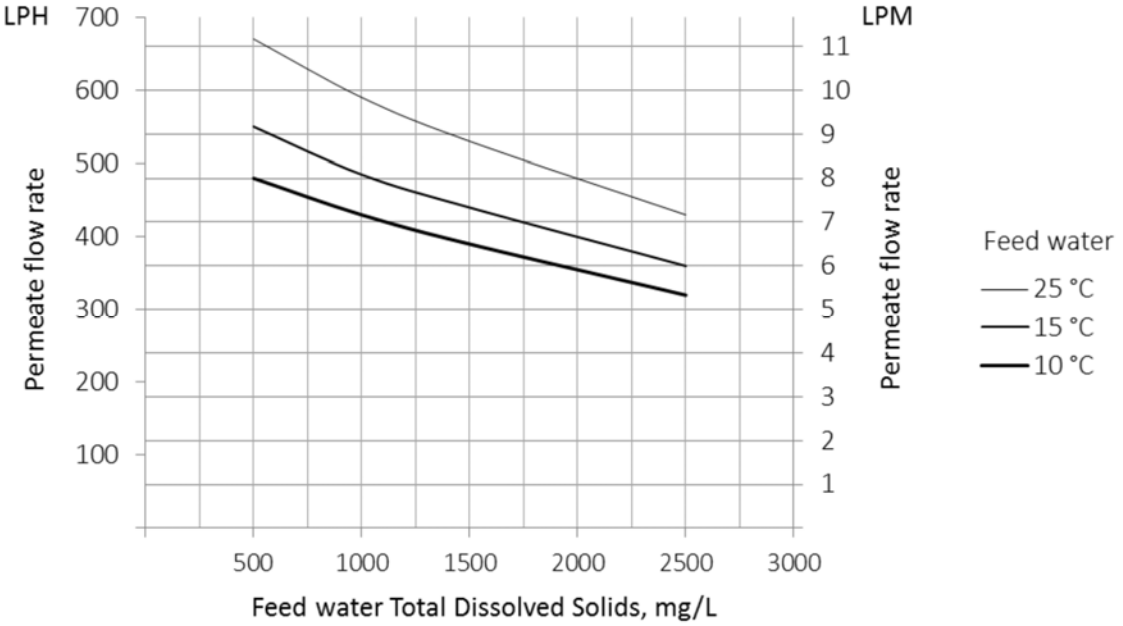
Raw water is fed through the polypropylene sediment filter (5 μm) to prevent particulate clogging of the membrane. High pressure pump feeds the pre-treated water into the membrane module, where spiral wound RO membrane element is installed. Recycle flow control throttles concentrate flow maintaining pressure inside the membrane module. Permeate exits the membrane module through the permeate outlet. Part of the concentrate is bled to drain; the rest is fed back to suction end of the high pressure pump via recycle line. Flow rates in recycle line and drain line can be manually adjusted with respective flow controls. Treated water is collected in a water tank. Float switch mounted in the tank halts the machine when the maximum level of permeate is reached. When the float switch is high, the controller first runs forward flush rinse then brings the machine to a halt. During forward flush, the membrane module is rinsed with raw water for 60 seconds.

Table 1: Standard operational parameters of the RO unit [8]

Unit capacity, m^3/d	**6**	**10**
Recycle flow rate, LPM	13-15	8.2-11.2
Drain flow rate, LPM	1.2-1.7	2.2-3.0
Permeate flow rate, LPM	3.5-4.5	6.5-9.0
Pressure in the membrane module, MPa	0.1-1.0	0.8-1.0



(a) Unit capacity 6 m^3/d



b) Unit capacity 10 m^3/d

Figure 8: Permeate flow rate – salinity curves for the RO unit [8]

Model water

The major water types being treated by RO/NF can be roughly characterized from the total dissolved solids (TDS) content that can be modeled with NaCl (technical grade).

Water type	Low saline	Medium saline		High saline
	Tap water	Ground water	Brackish water	Brackish water
TDS, mg/L	500	1500	5000	10000

Tasks performance order

General principle

The optimum operating pressure is determined by adjusting the feed pressure until the desired permeate quality and permeate flux rate are obtained. Sufficient feed flow should be maintained to ensure a low recovery rate (< 5%) as the membrane flux rate is increased. Permeate and concentrate streams are recycled back to the feed tank during the first test. The feed pressure at which the optimum permeate flux and permeate quality is obtained is the feed pressure used for the second test, determining the recovery rate.

Before Starting the RO Unit

1. Prepare model water solutions of different concentration, using NaCl and measuring final solution TDS with portable TDS-meter. Recommended concentration: 0.5, 1.5, 5, 10 g/L.

2. Calculate flow configuration:

Recovery, %	30	50	75	80
Permeate flow rate, L/h	Should be selected for the specific RO unit			
Drain flow rate, L/h				

3. Make preliminary checks to make sure all fittings are tight, all components are operational, and the feed solution is at the proper concentration. Before energizing the high-pressure pump, the low-pressure switch must be off for start-up to complete the circuit past the low-pressure cutout. Energize the high-pressure pump momentarily to check proper rotation.

RO Unit Operation

1. Ensure recycle and drain flow controls are fully open before starting the RO unit
2. Run the permeate tube to drain for the duration of the first run of the RO system
3. Switch on main circuit breaker to start the machine. After the controller starts up and RO unit starts operating, tighten drain flow control until drain rotameter reading meets experimental specifications.
4. Start turning down recycle flow control. This will raise pressure in the membrane module shown on pressure gauge. Stop when pressure in the membrane module meets experimental specifications.
5. After setting proper operating pressure, readjust drain flow rate (if it deviates in the process) to ensure that system operates with proper recovery according to the experimental conditions.
6. Make sure that the permeate flow rate and drain flow rate conform to your recovery calculation.
7. Let the RO unit run for 15 minutes discarding permeate and concentrate to drain. Watch pressure and flow rate readings to make sure these do not exceed requirements.
8. After 15 minutes, switch to experimental solution.
9. Record permeate flow rate for 3-5 different pressures for pure water.

Cautions

1. Take care not to exceed 1.6 Mpa in membrane module at any time. If membrane pressure rises above the upper limit in specification, open recycle flow control to bring it down.
2. Turn flow control knobs smoothly when regulating recycle and drain flow. Do not make rapid turns or apply disproportionate force as this can damage the RO unit.

Shutdown

Shut down by adjusting the by-pass valve or throttling valve to reduce the pressure, depressing the stop buttons on the high-pressure pump motor and the booster pump motor, and shutting off the feed supply valve (shutoff valve). When high concentrations (>5000 mg/L) are used, it is best to flush the reverse osmosis device with the feed solution to remove the high salt concentration in the device. This can be done by opening the concentrate flow control valve for approximately 10 min with at least 345 kPa (50 psi) feed pressure. Allow the pressure to reach zero before disconnecting the reverse osmosis device or carrying out maintenance on the piping system. Take care to ensure that the membranes are kept wet at all times and are properly sanitized or winterized, or both (based on supplier's recommendations) for long-term storage (more than 5 days).

Data collection and processing

The following data should be recorded during experimental operation:

- Date and time of RO unit operation
- Pressure drop per filter cartridge
- Feed temperature
- Feed, permeate and concentrate pressure
- TDS of the feed, permeate and concentrate streams
- pH of the feed, permeate and concentrate streams
- Observations

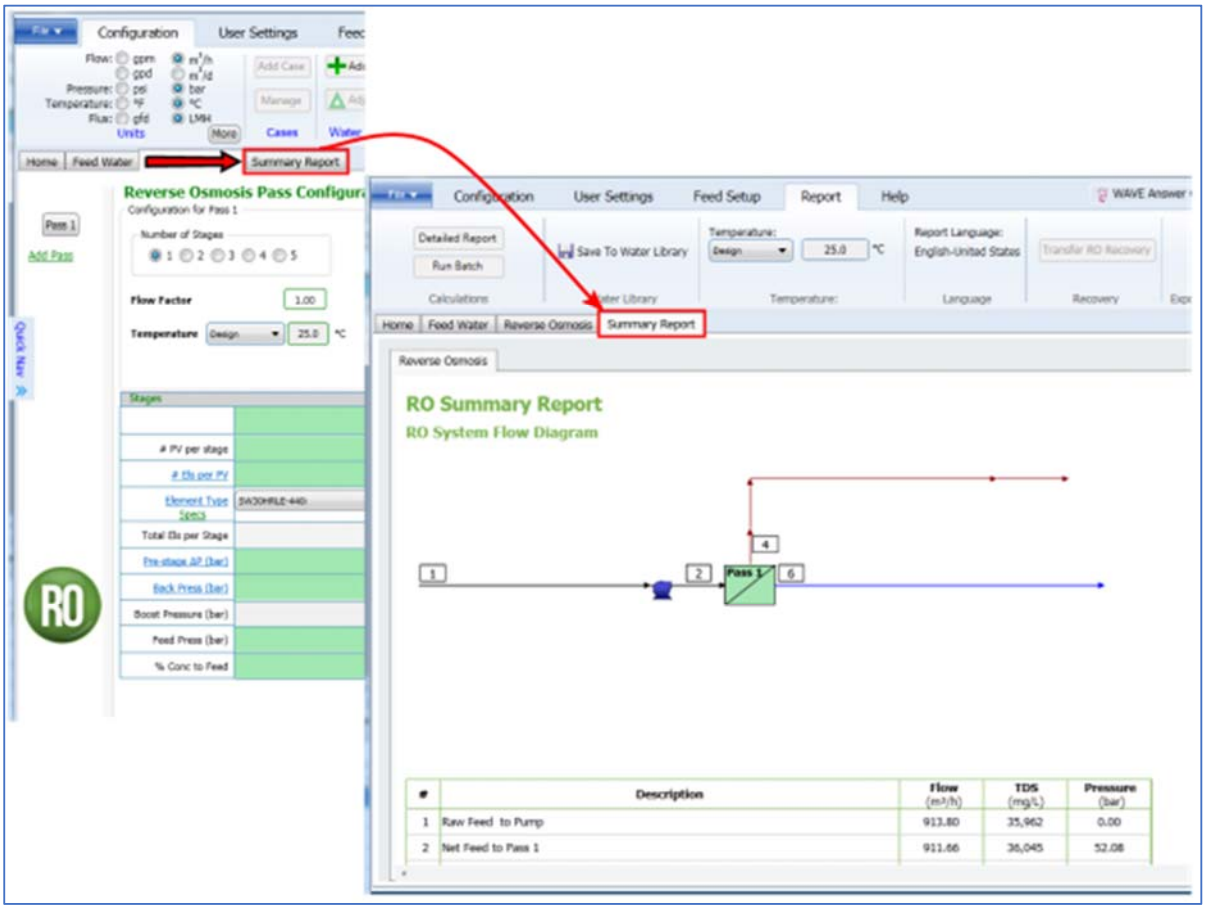
The performance of an RO unit is influenced by the feed composition, feed pressure, temperature and recovery. For example, a feed temperature drop of 4°C will cause a permeate flow decrease of about 10%, which is normal.

In order to distinguish between such normal phenomena and performance changes due to fouling or problems, the measured permeate flow and salt passage have to be normalized. Normalization is a comparison of the actual performance to a given reference performance while the influences of operating parameters are taken into account. The reference performance may be the performance specified by the membrane element producer in the Technical Data Sheet. Normalization has to be done following ASTM D 4516 standard (Appendix A).

Process modeling and data cross check

Membrane producers usually provide calculation software for modeling separation processes for their products. Therefore, it is possible to calculate RO operation parameters and crosscheck experimental data. For Filmtec membranes used in Ecosoft RO units, it is possible to do calculations in WAVE software that is available for free use https://www.dow.com/en-us/water-and-process-solutions/resources/design-software

It is necessary to input raw water TDS, membrane module type and RO unit operation parameters to the WAVE software and generate detailed report with hydraulic and concentrations results. The report will contain flow, TDS and pressure values for feed, concentrate and permeate flows.



#	Description	Flow (m³/h)	TDS (mg/L)	Pressure (bar)
1	Raw Feed to Pump	89.47	180	0.00
2	Net Feed to Pass 1	89.45	180	7.43
4	Total Concentrate from Pass 1	21.47	745	5.35
6	Total Permeate from Pass 1	68.00	1.01	0.00

RO System Overview

Total # of Trains	1	Online =	1	Standby =	0	RO Recovery	76.00 %
System Flow Rate	(m³/h)	Net Feed =	89.47	Net Product =	68.00		

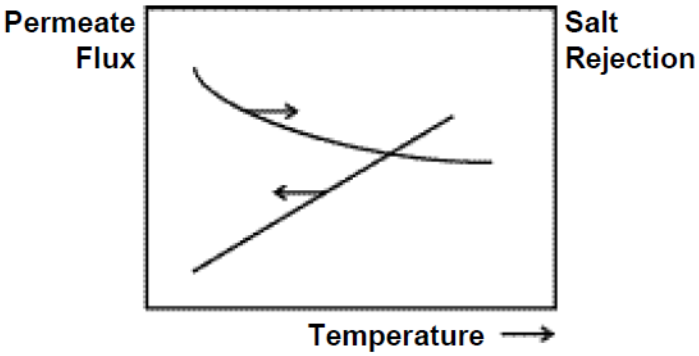
Pass	Pass 1
Stream Name	Stream 1
Water Type	Surface Water (SDI < 5)
Number of Elements	72
Total Active Area (m²)	2675.61

Report content

Results report shall include graphs of dependencies of permeate flux and salt rejection vs. pressure, recovery and feed concentration. The results obtained in the laboratory should be compared with calculation results from the modeling software (WAVE in case of Filmtec membranes)

Interpretation of results should be given with reference to the solution-diffusion model. For example, for temperature that is not considered as varying factor in this guideline, the results would have gotten the following interpretation:

- If the temperature increases and all other parameters are kept constant, the permeate flux and the salt passage are increasing due to (i) decrease of water viscosity and (ii) increase of polymer permeability.
- The graphs would have had the following look:



Questions

1. What are the objectives of the RO application testing?
2. Which quantities are to be set and measured in this work?
3. Where can you read the values of pressure and flow?
4. From where will you sample the solutions?
5. What is the purpose of bypass and safety valve? Where are they located?
6. Describe the procedure before starting and turning off the pump.
7. What pressure must not be exceeded and why?

Literature (recommended for reading)

Baker, Richard W., Membrane Technology and Applications, 2nd Edition, John Wiley & Sons, Ltd. (2004), Chapters 4 & 5.

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Geankoplis, Christie J., Transport Processes and Separation Process Principles, 4th Edition, Prentice-Hall (2003), Chapters 6 & 13

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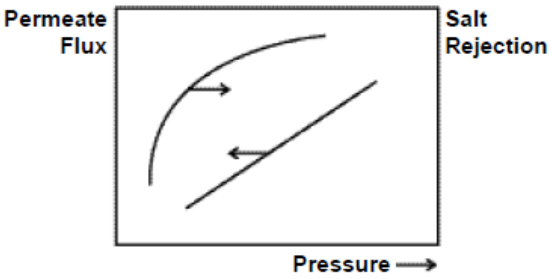
6. NALCO. Reverse Osmosis. https://www.slideshare.net/NelsonIzaguirre1/reverse-osmosis-module
7. Dow Filmtec Technical Manual
8. Ecosoft MO6000/MO10000 User Manual

Instructor's notes

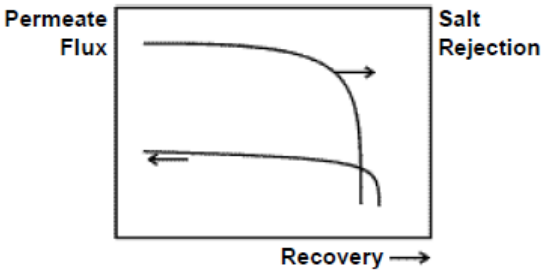
With increasing effective feed pressure, the permeate TDS will decrease while the permeate flux will increase.

Pressure:

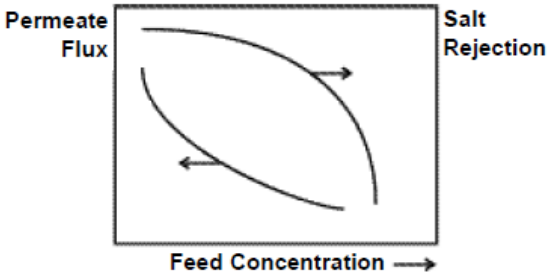


Recovery:

Recovery is the ratio of permeate flow to feed flow. In the case of increasing recovery, the permeate flux will decrease and stop if the salt concentration reaches a value where the osmotic pressure of the concentrate is as high as the applied feed pressure. The salt rejection will drop with increasing recovery.



Feed salt concentration:



4.3 Impact of the main parameters on the effectiveness of coagulation and the determination of the optimal dose of coagulant

Lab purpose

Study of regularities of the formation of the contact medium in the process of coagulation clearing the object of research and determining the optimal dose of coagulant based on waste alumina production.

Theory

Salts of aluminum and ferrum are most often used for coagulation purification of natural and sewage as coagulants.

The technology of water purification by coagulants consists of the following basic operations: pre-clarification, water purification, preparation and mixing of coagulant, discoloration and clarification.

In the case of the polydisperse composition of suspended matter, especially in the presence of coarse-dispersed coarse particles (sand, lobes of ore and non-metallic minerals), the wastewater is pre-clarified in horizontal tangential and aeration sand-traps with a circular or straight-line motion of water. Smaller mineral or organic particles are also separated by settling or filtration on slow filters filled with sand and gravel. Prefiltering on microfilters can be done in front of slow sand filters, before water treatment with coagulants or before rapid sand filters. As sedimentation structures, sedimentation ponds, horizontal tanks and their combination, as well as vertical, horizontal, radial, tubular, lamellar, etc. are used. The purified water is suspended if the alkaline reserve is insufficient for satisfactory hydrolysis of the coagulants.

Hydrogen and sodium carbonate. In the course the pH values are maintained within (6.5-7.5). It also contributes to reducing the residual content of aluminum and ferrum in purified water and reducing its corrosive properties. The clarification and discoloration of muddy waters with increased hardness by coagulants is expedient to carry out at high pH, and of colored soft waters - at reduced pH. Especially important is the order of the introduction of reagents. When the flotation reagents are added into the colored water before the addition of coagulants, the process of coagulation and cleaning quality has been deteriorated. In water, there is an increased content of stained substances. It is better to discolor the water in the case by adding of flotation reagents after of coagulants. Since some of the colored matter manages to absorb at the time of the formation of hydroxides. Organic substances contained in water in the form of humates of sodium, at low pH values are hydrolyzed to form negatively charged particles. The latter interact with positively charged polynuclear hydroxcomplexes (micelles). Therefore, in the case of treatment with coagulants of highly colored waters, they are subjected to flotation after coagulant administration.

One of the most important technological parameters of the process of water purification by coagulation is the dose of coagulant, its optimum value depends on the properties of the disperse system: temperature, the number of suspended and colloid dispersed substances, color, ionic composition of the dispersion medium, pH and other physico-chemical parameters. In the case of an insufficient dose of coagulant, the desired effect of cleansing is not achieved, and in the case of excess - in addition to over-consumption of a high-value reagent, in some

cases the effectiveness of coagulation may deteriorate. With a decrease in the temperature of treated water, the dose of coagulant increases significantly, especially in the case of muddy waters. With decreasing water turbidity, the temperature is lower. From the considerable content of suspended matter, they, coated with a "casing" of colloidal particles of aluminum hydroxide, coagulate, preventing the formation of long chain bridges from spherical particles. As a result, a smaller dose of coagulant is required. For high-infused waters with an increase in their alkalinity, the dose of coagulant increases, for turbid - decreases.

To coagulate quickly and throughout the volume of purified water, it is necessary to mix the reagents vigorously over a short period of time (1-2 minutes in the case of wet and no more than 3 minutes - dry dosage of reagents) in hydraulic or mechanical mixers. The mixing of the coagulant with water should occur so that a large number of small aggregates originally formed on the surface, on which chemoresubbed charged polynuclear hydroxocomplexes of aluminum having high activity relative to the impurities to be purified. In a one-stage technological scheme, the coagulant is added in the immediate proximity of the filters.

It is desirable to introduce the reagent into a relatively small amount of purified water, and then quickly mix it with the rest (separate coagulation). An increase in the initial concentration of coagulant contributes to the intensification of the coagulation process due to an increase in the partial concentration of coagulant in the treated volume of water (concentrated coagulation). Sometimes we recommend the ratio of volumes of treated and untreated water to 1: 1.5. In the case of concentrated coagulation, the cost of ferrous sulfate is reduced by 20-30%, as well as the turbidity and color of water are reduced.

Effective process is fractionated (fractional or partial) coagulation of water, in which the coagulant is added to the water to be purified in two or more portions or successively introducing different coagulants. In this case, polydisperse aggregates of the coagulant are formed, as well as the period of formation of positively charged polynuclear hydroxocomplexes, resulting in coagulation intensified. The recommended optimal time interval between the introduction of individual parts of the coagulant is 90 - 120 seconds. In the case of discoloration of water, the first dose of coagulant should be half the total.

Periodic coagulation is based on a combination of methods of concentrated and fractionated. The feeding periods of increased doses of coagulant alternate with periods of complete cessation of coagulation. As a result of such treatment of low-purity water for a two-stage scheme, the cost of coagulant is reduced by 30 - 40%, the degree of discoloration of water rises. Deeper removal of coloring impurities is due to lower pH values during the feeding of increased doses of coagulant.

Coagulation inactivation is also achieved by recirculation of coagulant (coagulated curvature). The essence of the method is to supply part of the spent siege to the zone of dosage of fresh portions of the coagulant. This helps to accelerate the process and form denser flakes. The application of this method is effective for the intensification of coagulation of low-wasting waters, while significantly (up to 30%) the costs of coagulant are reduced.

The process of formation of flakes successfully occurs with a slow and even mixing of the disperse system, which helps to agglomerate the small flakes into larger ones that easily deposit. It is especially necessary to mix at low temperatures of treated water (below 5 ° C). During the mixing, the growth of the particles is accelerated as a result of their collision, the interconnection increases and solid flakes are formed. Mixing positively influences the formation of flakes in the event that the particles have reached a certain size as a result of the Brownian motion (spherical aggregates larger than 0.02 microns and larger).

The mixing of water should not be too intense to prevent the destruction of flakes. In order to ensure optimal mixing conditions in front of the septic tanks, flush cameras are often arranged in which the vertical or horizontal movement of water is provided by means of partitions or whirlpool devices.

The formed coagulant flakes, together with the adsorbed impurities, are separated from the water to be purified during clarification by means of defending, filtering, centrifuging or floating. In the practice of water preparation, the suspended matter is first separated by settling, and then the drains are filtered. Horizontal, vertical or radial tanks are usually used.

Equipment and reagents

Equipment

Flasks are nominal volume of 100 cm^3 - 6 pcs, volume 50 cm^3 - 6 pcs; the flask measures a nominal volume of 1000 cm^3; the flask measures a nominal volume of 250 cm^3 - 2 pcs; spatula; Pipettes with a nominal volume of 1, 2, 10 cm^3; sampler; photoelectrocolorimeter type KFK - 2; cuvettes; scales analytical, litmus paper.

Reagents

A mixture of ammonium molybdate, sulphatic acid, stybium chloride and tartaric acid. Up to 300 cm^3 of palladium acetate is stirred with 144 cm3 of concentrated sulfuric acid, ppm. It is then cooled to 20 ^oC and, when stirred, add a solution of 10 g of sulfamic acid NH_2SO_8H pda. and 100 cm^3 of distillate solution, 12.5 g of ammonium molybdate $(NH_4)_2Mo_7O_{34} \cdot 4H_2O$ in 200 cm^3 of distillate solution, 0.235 g of sitbium chloride of $SbCl_2$ pda a. and 0.6 g of tartaric acid odd.a. in 100 cm3 of distillate. The icons are kept in a glass of orange glass.

Ascorbic acid. 10% solution. Dissolve 10 g of ascorbic acid in bistystilate and bring the volume of solution to 100 cm3 in a measuring dish. Store the solution in the cold, stable for about 30-40 days.

Potassium phosphate monosubstituted - standard solution.

Basic solution: Dissolve 0,7165 g of KH_2PO_4 pda, dried for 2 hours at a temperature of 105 oC, in a distillate. Add 2 cm3 of chloroform and bring the volume of the solution with distillate to 1 dm3 in a volumetric flask. 1 cm3 of this solution contains 0.389 mg of phosphate.

Working solution 1: Make 10.0 cm^3 of the basic solution to 250 cm^3 of distillate. Use freshly prepared solution. 1 cm3 of this solution contains 0.0156 mg of phosphate.

Working solution 2: Make 50,0 cm^3 working solution 1 to 250 cm^3 distillate. Use freshly prepared solution. 1 cm3 of this solution contains 0.00312 mg of phosphate.

Plotting of the calibration graph

In a volumetric flask with a capacity of 50 cm3 are placed 0; 1; 2.5; 5; 10; 25 cc of working solution 2. Add 2 cc of a solution of the mixture, 0.5 cc of 10% solution of ascorbic acid to each flask. The mixture is brought to the mark with a distillate and stirred. The first bulb (without the content of the working solution 2) - "idle experiment". After 20-25 minutes photometrically in a cell 10 mm in wavelength 670 nm and based on the data we build a calibration graph "Optical density - concentration of phosphates". An example of the calibration graph is shown in Figure1.

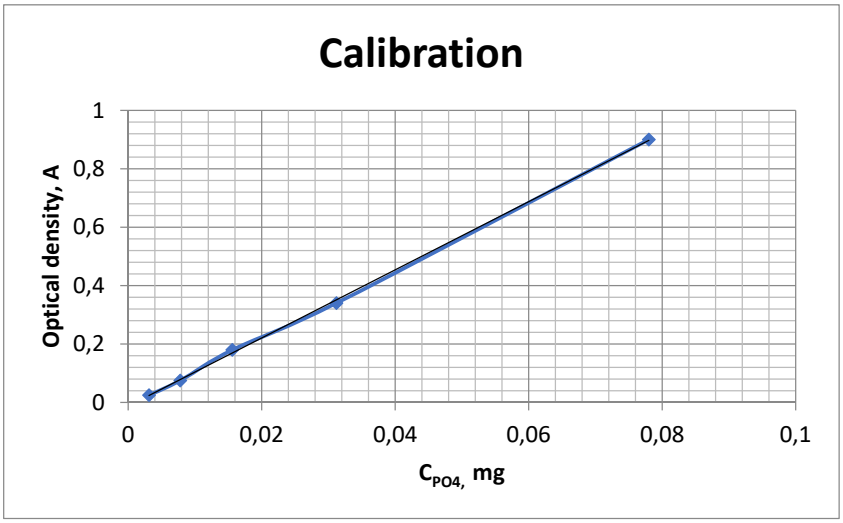


Figure 1: Calibration graph

Tasks performance order

Determination of the efficiency of removal of phosphates by coagulation method, selection of the optimal dose of coagulant.

Experiment 1**: Coagulation at pH 9 (NaOH substrate reagent).**

For study use working solution 1. In 4 cylinders of coagulation pour 100 cm^3 of the test solution. Then add a dose of coagulant (a solution of sulfate or iron chloride) to the pipette so that its content in water is 25, 50, 75 and 100 mg / dm^3. Using a solution of sodium hydroxide, the pH of the solution is adjusted to 9-10. After mixing the three-fold turning of the closed cylinder caps, the time of entering the coagulant in water is noted. After 30 minutes, water from each cylinder is filtered through a "blue ribbon" filter in conical flasks. To analyze the coagulation efficiency, the filtrate is diluted similarly to the preparation of the solution for preparation of the calibration: 5 cm^3 from each cylinder in a 100 cm^3 flask and brought to the label with a distillate. From the obtained solutions, an aliquot of 5 cm^3 is drawn into a 50 cm^3 flask, 2 cm^3 of a mixture solution, 0.5 cm 3 of ascorbic acid is added and distilled to the label. After 20-25 minutes, photometrically, and on the basis of the obtained value, the residual concentration of phosphate in the solution is found on the graph.

WARNING! Time to settle solutions before photometry should be the same for all experiments.

Experiment 2**: Coagulation with the addition of CaO as a subletting reagent.**

For study use working solution 1. In 4 cylinders of coagulation pour 100 cm^3 of the test solution. Then add a dose of coagulant (a solution of sulfate or iron chloride) to the pipette so that its content in water is 25, 50, 75 and 100 mg / dm^3. On technical scales weigh 0.3-0.5 g CaO. After the introduction of the coagulant and CaO, the solution is mixed with a three-fold reversal of closed cylinder cams. Mark the time when the coagulant is injected into the water. After 30

minutes, water from each cylinder is filtered through a "blue ribbon" filter in conical flasks. To analyze the coagulation efficiency, the filtrate is diluted similarly to the preparation of the solution for preparation of the calibration: 5 cm3 from each cylinder in a 100 cm^3 flask and brought to the label with a distillate. From the obtained solutions, an aliquot of 5 cm^3 is drawn into a 50 cm^3 flask, 2 cm^3 of a mixture solution, 0.5 cm^3 of ascorbic acid is added and distilled to the label. After 20-25 minutes, photometrically, and on the basis of the obtained value, the residual concentration of phosphate is found on the directory.

Report content

Removal degree of phosphates, %:

$$X = \frac{Cv - Ck}{Cv} \cdot 100\%,$$

where *Cv* – initial concentration, g/dm^3;

Ck – final concentration, g/dm^3.

Make conclusions about the effectiveness of the dose of coagulant and the conditions for coagulation.

Discussion issues

1. Provide the conditions (mode) of the formation of the contact environment in the suppressed state.
2. How does the characteristic of treated water affect the efficiency of the process?
3. Under what conditions depends on choosing the type of coagulant?
4. Give the types of luminaries and the principle of their operation.
5. Describe the loading of filters used in water treatment technology
6. Types of filters and the principle of their operation.

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4.4 The dynamic exchange capacity of cation exchanger

Lab purpose

The purpose of this lab work is to determine the dynamic exchange capacity of cation exchanger, until the penetration of Ca^{2+} ions into the filtrate and to regenerate cation in co-current mode by the solution of sodium chloride and to wash up it by distilled water.

Theory

The essence of ion exchange is the solid (liquid) substance (resin) absorbs anions or cations from electrolyte solution, changing it on equivalent quantity of other ions with the same charge sign. There is the classification on anion exchangers and ampholytes. The exchanged ions are classified on cation and anion exchangers.

There are artificial high molecular organic ion exchangers. Poly electrolytes are almost undissolved in water and other solvents. The possibility of ion exchanging is caused by availability of active ion groups with moveable ions (counter ions) in ion exchangers. They can be exchanged on ions of environment. If this active groups have acidity character, ion exchangers (cation exchangers) are capable to change moveable hydrogen or sodium ions on other cations from electrolyte solution. If the functional groups have alkalinity properties, ion exchangers change moveable hydroxide ions on other anions.

The certain polymer determines the space structure of ion exchanger. Cells consist of the matrix. These are high molecular, ion exchange materials and moveable ions, which are almost insoluble in water and other solvents. The last one's caused the charge of certain signal. The ion exchange process can be described by reversible equilibrium heterogeneous chemical reactions of double exchange:

$H[Kat] + Na^{+} = Na[Kat] + H^{+}$;

$2Na[Kat] + Ca^{2+} = Ca[Kat]_2 + 2Na^{+}$;

$[An]OH + Cl^{-} = [An]Cl + OH^{-}$;

$2[An]OH + SO_4^{2-} = [An]_2SO_4 + 2OH^{-}$; where [An] – anion exchanger; [Kat] – cation exchanger.

The most important characteristic of ion exchange sorbents is full exchange capacity. This is the theoretic number of ionic groups, containing in the single mass or volume of the ion exchanger.

The capacity is quantity of sorbed ion by the specific mass or volume of the ion exchanger in equilibrium conditions (mmole/g, mmole/L). It can be determined in static and in dynamic conditions. The static exchange capacity is determined by contacting the mass of ion exchange material with certain volume of the investigated solution, until the equilibrium. The dynamic exchange capacity is the quantity of ions, absorbed by the same mass of ion exchange at continuous flowing of the electrolyte solution through the layer of ion exchange resin, until the penetration of ions. The full dynamic exchange capacity is determined by flowing of solution through the column of knowing quantity of the ion exchanger, until the composition of filtrate and inlet solution become the same. The ion exchange reactions are reversible. That's why, if the concentration of ions H^{+}, Na^{+}, OH^{-} is increased extremely, the equilibrium moves to the left. This property is used at the regeneration of ion exchangers.

Equipment and reagents

Equipment: volumetric flasks (100 cm^3); volumetric cylinders (250 cm^3) – 2 ones; pipettes (100 cm^3); glass columns; bulbs for the titration (volume 250 cm^3).

Reactants: cation exchanger; working solutions of $CaCl_2$ (8 % mass) and NaCl (8 % mass), ammonia buffer solution; the indicator – chrome dark blue; 0.01 mole/L solution of Trilon B; argentum nitrate solution.

The installation of the dynamic exchange capacity of cation exchanger determination (fig 1.) consists of ion exchanger column-filter 1, presented by glass tube (diameter 15…25 mm); the bottom part of it includes glass diaphragm 2 for supporting of ion exchange resin layer 3. The cation exchanger quantity in column is 30 g. The glass taps and Mor's clamp on resin tube is designed for the regulation of liquid rate in the bottom part of column. From above the column is closed hermetically by resin tube with hole 5. For entering the investigated solution of $CaCl_2$, NaCl solution to the column for regeneration of ion exchanger and water for washing up, the glasses 6 – 8 are set up. The reactants are entered for score of hydrostatic pressure from it., The volumetric cylinder 9 is used, for the determination of solution quantity, moving through column.

Tasks performance order

Experiment 1. **Ion exchange filtration of calcium chloride solution**

The filtration rate of solution through the cation exchange filter is regulated at the beginning. Distilled water is passed through the filter from top to bottom. The regulation of flow rate is carried by regulated device 4. The time is determined by passing 20…25 cm^3 of water, accumulated in volumetric cylinder 9. When liquid flow achieves necessary rate, the tap is closed. The linear rate of filtration should be approx. 5 m/hour.

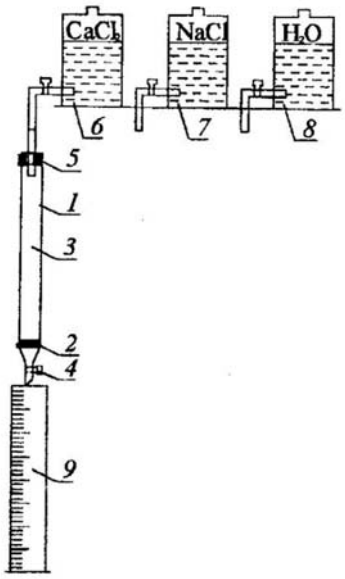


Figure 1: The installation for the determination of dynamic exchange capacity of cation exchanger: 1 – column-filter; 2 – glass diaphragm; 3 – ion exchange resin; 4 – clamp or tap; 5 – stopper with hole; 6 – 8 – glasses with solutions and water; 9 – volumetric cylinder

When the speed of liquid pouring has been determined, the solution of calcium chloride with molar concentration of equivalents 3.5 mmole/L is filtrated. The column with ion exchanger, instead of glass with distilled water 8, the glass 6 with $CaCl_2$ is connected. Then the tap is opened and filtrate is picked up by portions (100…110 cm^3). The concentration of calcium cations is determined in it by complexonometric method. The filtration is stopped when the concentration of calcium ions in filtrate achieves above 0,05 mmole/L. After this the summary volume of filtrate has been passed through the ion exchange layer can be determined.

Figure 2: The photo of installation for the determination of dynamic exchange capacity of cation exchanger

Experiment 2**. The regeneration and washing up of the cation exchanger**

The glass 7 with solution of sodium chloride (mass fraction – 8 %) is connected to the column. It is passed through the layer of ion exchanger. The volume of NaCl solution should include the summary volume of $CaCl_2$ solution, passed through the column with the same rate. Then excess of salt solution is washed up by connecting glass 8 with distilled water to the column. It is washed up, while water for washing would not contain chloride ions (sample with argentum nitrate). It's necessary to use not less than 1000 cm^3 of distilled water.

Report content

The determination of content of calcium ions in filtrate is based on the reversible reaction

$Ca^{2+} + H_2Y^{2-} = CaY^{2-} + 2H^+$,

where H_2Y^{2-} - anion of Trilon B.

The reaction charged in alkaline buffer mixture (at pH 10), neutralized hydrogen ions, for moving the equilibrium to the formation of complex CaY^{2-}.

100 cm^3 of the filtrate is picked up (105...110 cm^3). Then 5 cm^3 of ammonia buffer solution and 2...3 drops of indicator are added into conical bulb with capacity 250 cm^3 by pipette or volumetric flask. The liquid is mixed and titrated by Trilon B solution from crimson to violet blue color.

The content of calcium ions is calculated by the formula:

$$C_{Ca^{2+}} = \frac{V_1 \cdot C_{H_2Y^{2-}} \cdot 1000}{V},$$

where $C_{Ca^{2+}}$ is the concentration of calcium ions in filtrate, mmole/L; V_1 – volume of Trilon B solution spent for the titration, cm^3, $C_{H_2Y^{2-}}$ is the concentration of Trilon B solution, mole/L; V –volume of water sample, cm^3.

The experimental data is recorded to the table.

Table 1: The experimental data

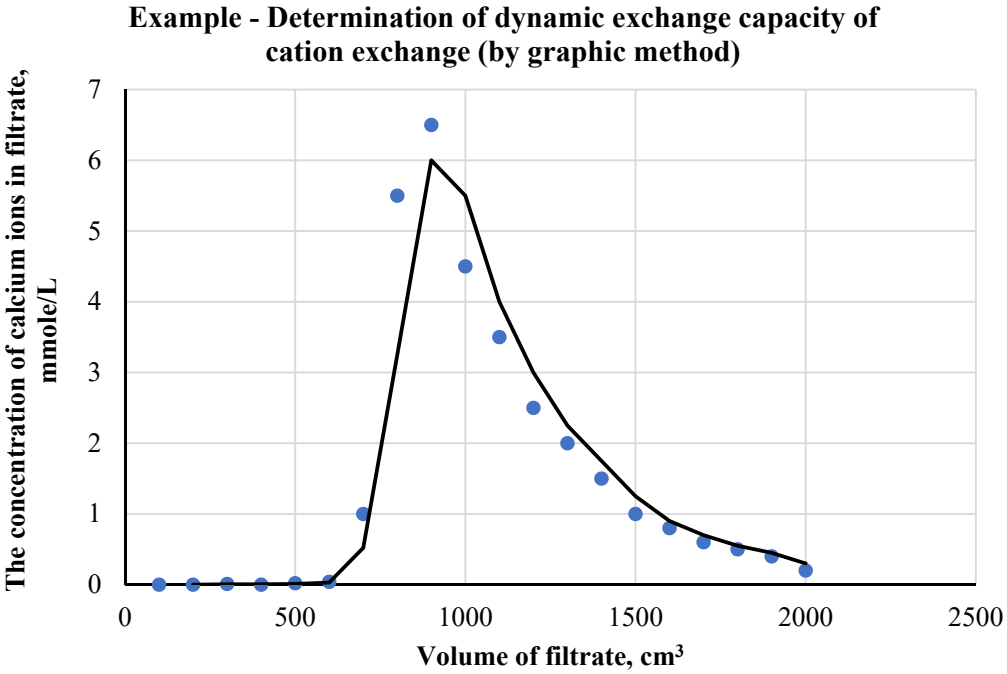
Number of sample	Volume of sample, cm^3	The volume of electrolyte passed through the filter, cm^3	The concentration of calcium ions in filtrate, mmole/L

It's necessary to build filtration curve in coordinates "electrolyte volume passed through the filter – calcium ions concentration in filtrate" and to determine the filtrate volume until the penetration of calcium ions by it. The penetration concentration of calcium ions equals 0,05 mole/L.

The dynamic exchange capacity is calculated by the formula

$$DEC = \frac{V_{pen} C_{Ca^{2+}}}{1000 \cdot m},$$

where *DEC* is the dynamic exchange capacity of cation exchanger, mmole/g; V_{pen} is the volume of filtrate until the penetration of calcium ions, cm^3; $C_{Ca^{2+}}$ is the concentration of calcium ions in filtrate, mmole/L; *m* is mass of cation exchanger, g.



Discussion issues

1. Explain the essence of ion exchange. Write down equations of reactions.

2. Describe the structure and properties of artificial ion exchangers (moveable ions, exchange capacity, swelling, acidity-alkalinity properties, osmotic stability etc.).

3. How the dynamic exchange capacity of ion exchangers can be determined?

4. What the essence of the regeneration of ion exchangers?

5. Call the spheres of using ion exchange in water treatment processes. What are its preferences and drawbacks comparing with other methods?

6. Present the principal scheme of softening and desalination of water by ion exchange method. What requirements are to water quality in different branches of industry?

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4.5 Evaluation of the carbonic-acid equilibrium

Lab purpose

At performing of this lab work, you will study the alkalinity and buffering capacity of several types of water: surface water, groundwater (mineral water) and sea water. You will observe shifting of carbonate content vs. the source of water sampling. You will get experience to calculate the kind of alkalinity in different waters. You will determine the buffering capacity in selected water samples by titration method.

Theory

Of all acid-base systems, the most important is the system encompassed CO_2, HCO_3^-, and CO_3^{2-}. Interconversions of these carbonate containing compounds cover a huge scale of nature, from the operation of the global carbon cycle till the pH balance of blood cellular fluids, the hardness of raw water and its alkalinity. The water used everywhere and in particular to cool equipment. The reason for frequent violations and sometimes accidents with the work of cooling equipment is the unsatisfactory quality of the cooling water, namely its instability. Instability can be of two types: aggressive and which lead the formation of precipitation in the pipelines. Therefore, it is very important to control the content of carbonic acid and its derivatives in water.

The carbonate system embraces virtually all of the environmental compartments: the atmosphere, hydrosphere and lithosphere. The complementary processes of photosynthesis and respiration drive a global carbon cycle. In this cycle, carbon passes slowly between the atmosphere and the lithosphere, and more rapidly between the atmosphere and the hydrosphere as shown on Figure 1.

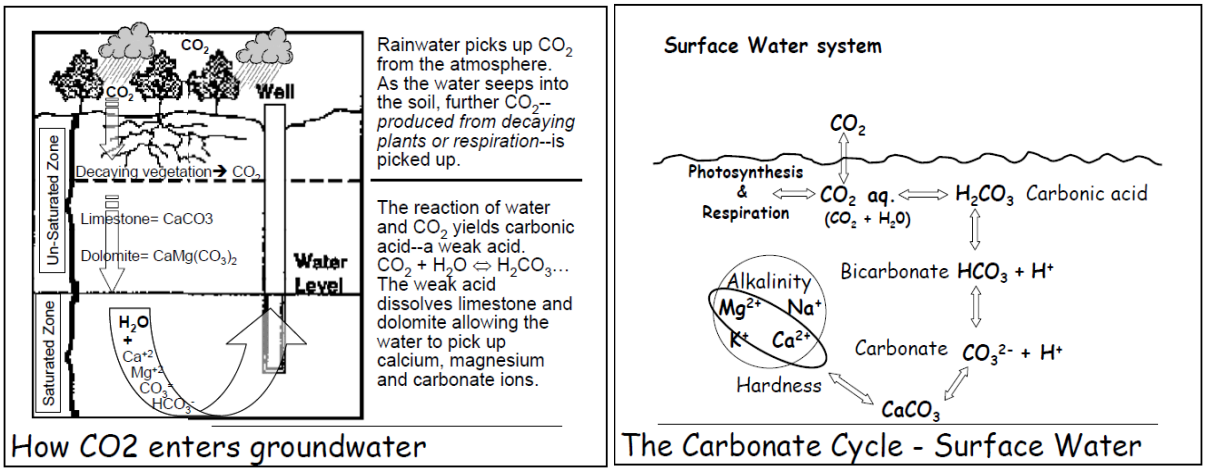

Figure1: Schematic representation of carbonate cycle in Nature.

At present, the volume-percent of CO_2 in atmospheric air is about 0.04%, leading to a partial pressure of ≈ $4*10^{-4}$ atm. In a crowded and poorly ventilated room, P_{CO2} can be as high as 100 $\cdot 10^{-4}$ atm. About $54 \cdot 10^{14}$ moles ($2.4 \cdot 10^{11}$tones) per year of CO_2 is removed from the atmosphere by photosynthesis, divided about equally between land and sea. All of this, except

0.05% comes back to biosphere by respiration (mostly by microorganisms). The remainder comes into sedimentary part of the geochemical cycle where it can remain for thousands to millions of years.

Since the advent of large-scale industrialization around 1860, the amount of CO_2 in the atmosphere is increasing continuously. Most of this is due to fossil-fuel combustion; Large-scale destruction of tropical forests, which has accelerated greatly in recent decades do exacerbate this effect. At present about 30-50% of the CO_2 released into the atmosphere by combustion remains there; the remainder enters the hydrosphere and into the soil of lithosphere as shown on Figure 1.

The oceans have a large absorptive capacity for CO_2 by virtue of its transformation into bicarbonate and carbonate in a slightly alkaline aqueous medium, and they contain about 60 times as much inorganic carbon as it is in the atmosphere. In addition to atmospheric CO_2, there is a carbon input to oceans from streams. This input is in the form of CO_3^{2-}, which derives from the weathering of rocks and terrestrial carbonate sediments, and gives rise to the acid-base reaction:

$$H_2CO_3 + CO_3^{2-} \rightarrow\!| \quad 2HCO_3^- \qquad (1)$$

In such a way, the Earth ocean, is the site of a gigantic acid-base titration in which atmospheric acids (mainly CO_2 but also SO_2, HCl and other acids) interacts with carbonates of mineral rocks and particles of wind blown dust. Carbon dioxide is slightly soluble in water. Its solubility in the range of 0°C - 20°C decreases from 0.077 mol/liter to 0.039 mol/liter.

In the presence of gaseous CO_2, dissolved CO_2 exchanges with CO_2 gas according to equations:

$$CO_2(g) + H_2O \leftrightarrows CO_2(aq) + H_2O \qquad (2)$$

and

$$CO_2(aq) + H_2O \leftrightarrows H_2CO_3 \qquad (3)$$

where (g) and (aq) refer to the gaseous and aqueous phases, respectively.

Dissolved carbon dioxide consists mostly of the hydrated oxide $CO_2(aq)$, i.e.($CO_2 \cdot H_2O$). It coexists with a small portion of carbonic acid. The relationship is following:

$$[CO_2(aq)] \approx 650\ [H_2CO_3] \qquad (4)$$

Concentration of $CO_2(aq)$ far exceeds that of dissolved H_2CO_3 as shown by equation 4. The total concentration of $[CO_2aq]$ and $[H_2CO_3]$ in water considered as concentration of dissolved CO_2, so:

$$[CO_2aq] + [H_2CO_3] = a. \qquad (5)$$

In this mixture, H_2CO_3 dissociates according to equations:

$$H_2CO_3 \leftrightarrows H^+ + HCO_3^- \qquad (6)$$

and

$$HCO3^- \leftrightarrows H^+ + CO3^{-2} \qquad (7)$$

where the equilibrium conditions are quantified by the dissociation constants:

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} \quad (8)$$

and

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \quad (9)$$

The values of dissociation constants K_1 and K_2 at 25^0C in the fresh surface water are equal to $4.498 \cdot 10^{-7}$ and $4.79 \cdot 10^{-11}$ consequently.

Here we have to emphasize, that although the hydrogen ion, H^+, commonly exist in hydrated state to form H_3O^+ it adopted to write the hydrated hydrogen ion as H^+ since the hydrated structure does not enter the chemical models. The $[H^+]$ concentration generally given as a pH value, defined as the negative logarithm of $[H^+]$, i.e.:

$$pH = -\log [H^+] \quad (10)$$

In such a way the total concentration of dissolved inorganic carbon (C_T) in the any water sample defined by the sum:

$$C_T = [CO_2aq] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] = a + b + c \quad (11)$$

Where:

$[CO_2aq] + [H_2CO_3] = a$;

$[HCO_3^-] = b$,

$[CO_3^{2-}] = c$.

Concentration of each depicted carbon-containing substances in different waters and relationships among these substances are functions of the partial pressure of CO_2 in the atmosphere, the concentration of different minerals dissolved in water, and of water temperature.

So, the studying of carbon composition of water, whether it concerns freshwater, sewage water or seawater, is a complicated task. To be able to get success one need to know the properties of the following compounds:

- gaseous CO_2 (CO_2 g) with its partial pressure (PCO_2) in the atmosphere;
- dissolved CO_2 (denoted by CO_2aq.);
- dissolved carbonic acid, H_2CO_3 with concentration “a” = $[H_2CO_3]$ + $[CO_2aq.]$;
- dissolved bicarbonate, HCO_3^- with concentration “b” = $[HCO_3^-]$;
- dissolved carbonate, CO_3^{2-} with concentration “c” = $[CO_3^{2-}]$;
- total dissolved inorganic carbon, with concentration C_T = a + b + c;
- concentration of other solutes which affect the degree of dissolution and ionization of carbonate containing compounds in water;

Quantitative analysis of carbonate system in different waters is based on calculation “effective” concentration of $[CO_2aq]$, $[H_2CO_3]$, $[HCO_3^-]$, $[CO_3^{2-}]$ and their influence on each other as function of pH, temperature (^{o}C) and concentration of all inorganic solutes present in water.

Performing this work, the specialists operate with activity (a) of dissolved substances instead of their formal concentration. Activity is much smaller of concentration in the presence of essential amounts of salts dissolved in water. The basic analytic equations are following:

$$K_0 = \frac{a_{H_2CO_3}}{P_{CO_2}} = \frac{\gamma_a [H_2CO_3]}{P_{CO_2}} \tag{12}$$

Here the activity coefficient γ <1 (γ = 1 when solutes concentrations are very low.)

When seawater or brackish water is studied, more practical is to describe the relation between actual and theoretical concentration by the apparent solubility constant like shown here:

$$K_0' = \frac{[H_2CO_3]}{P_{CO_2}} = \frac{K_0}{\gamma_a} \tag{13}$$

Respectively, the thermodynamic and the apparent dissociation constants of the first dissociation step of carbonic acid expressed as follow:

$$K_1 = \frac{a_H \cdot a_{HCO_3}}{a_{H_2CO_3}} = \frac{\gamma_H [H^+] \cdot \gamma_b [HCO_3^-]}{\gamma_a [H_2CO_3]} \tag{14}$$

and

$$K_1' = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = \frac{\gamma_a}{\gamma_H \cdot \gamma_b} K_1 \tag{15}$$

And the constants of the second step of dissociation are expressed as:

$$K_2 = \frac{a_H \cdot a_{CO_3}}{a_{HCO_3}} = \frac{\gamma_H [H^+] \cdot \gamma_c [CO_3^{2-}]}{\gamma_b [HCO_3^-]} \tag{16}$$

and

$$K_2' = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = \frac{\gamma_b}{\gamma_H \cdot \gamma_c} K_2 \tag{17}$$

Having these expressions, the relative concentrations of $[H_2CO_3]$, $[HCO_3^-]$ and $[CO_3^{2-}]$ one can found by next manner:

$$[H_2CO_3] = K_0 P_{CO_2} \tag{18}$$

$$[H_2CO_3] = \frac{[H^+]}{K_1} [HCO_3^-] \tag{19}$$

$$[CO_3^{2-}] = \frac{K_2}{[H^+]} [HCO_3^-] \tag{20}$$

So that:

$$C_T = \left(\frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]} \right) [HCO_3^-] \tag{21}$$

And the fractional concentration of $[H_2CO_3]$, $[HCO_3^-]$ and $[CO_3^{2-}]$ can be given in terms of the total carbon content like shown below:

$$[HCO_3^-] = \frac{[H^+]K_1}{[H^+]^2 + [H^+]K_1 + K_1K_2} * C_T \tag{22}$$

$$[H_2CO_3] = [CO_2aq] = \frac{[H^+]^2}{[H^+]^2 + [H^+]K_1 + K_1K_2} * C_T \tag{23}$$

$$[CO_3^{2-}] = \frac{K_1K_2}{[H^+]^2 + [H^+]K_1 + K_1K_2} * C_T \tag{24}$$

The magnitudes of K_0, K_1 K_2 of carbonic acid in freshwater, and K_0' K_1', K_2' in mineralized water are differed essentially.

The difference in values of K_0 , K_1, K_2 and K_0', K_1', K_2' leads to distribution of H_2CO_3 and of its dissociation products in fresh water and in seawater like shown on fig.2.

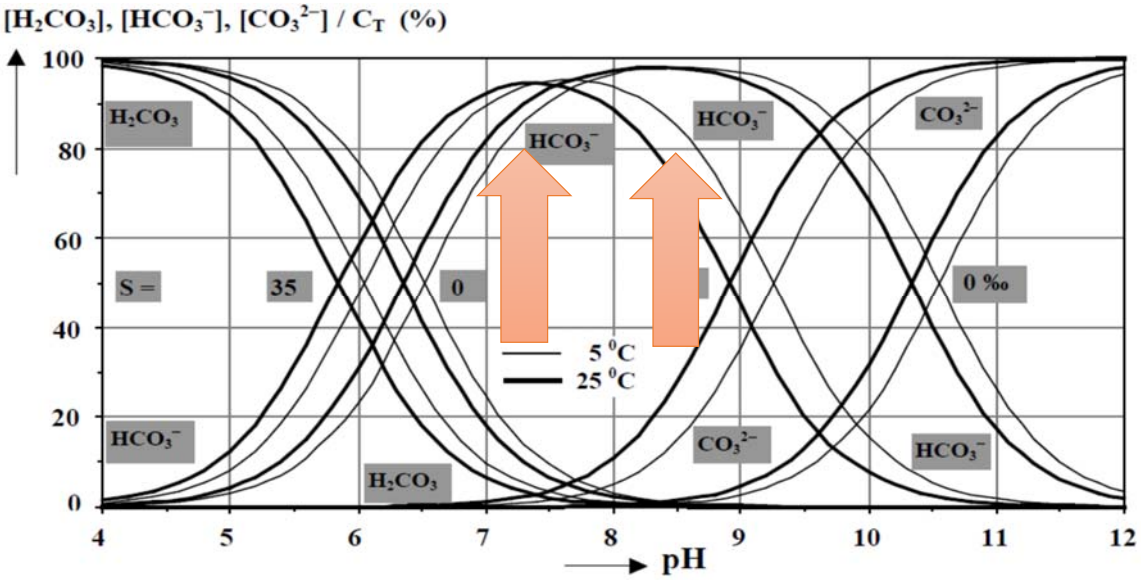

Figure 2: Distribution of the carbonic acid fractions as percentages of the total carbon content, C_T for temperatures of 5^0C and 25 ^{0}C and for salinities of 0% and 3,5 % vs. pH.

On this figure arrows with indexes of "1" and "2" depicts of maximal HCO_3^- concentration when salinity of water is zero and 3,5% consequently. One can see also the pH values when the concentration of H_2CO_3 and CO_3^{2-} becomes gone as well as that pH values when the concentration of these substances reaches of maximum. So, Figure 2. show in details the difference in distribution of carbonic acid fractions vs. pH, salinity of water and its temperature.

The sum of the concentration of carbonic acid and its fractions in water named the alkalinity of water.

The alkalinity of water represents its ability to neutralize inputs of acids. For natural water the alkalinity is most important in the context of inputs of acids caused by human activities; e.g., acid rain, acid mine drainage, excessive fertilization with ammonium etc.

Alkalinity is an important consideration in waters used for drinking and industrial applications, as well as in the cases of raw water and wastewater treatment. Most microorganisms can function best at neutral pH values. So, when the pH of water shifts outside of optimal range (e.g., through denitrification, nitrification, anaerobic fermentation reactions) the run of water treatment processes can be affected disastrously. The oxidation of Fe^{2+} that results when anaerobic ground waters are exposed to air can cause a marked acidification of water that are poorly buffered with alkalinity; As the result arisen acidity enhance the pipes corrosion.

The simplest method to study alkalinity of water is its acid titration up to certain endpoints taking into account that alkalinity (A_T) is a quantity of HCO_3^-, CO_3^{2-} and OH^- ions following from the preservation of electroneutrality in the water samples where the metal-ion concentrations (Na^+, Ca^{++}, Mg^{++}, etc.) and pH are constant, i.e.:

$$A_T = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \quad (25)$$

In (25) participation of other weak acids may also be included in the interest of high precision, such as humus acids in freshwater, or borate, $[B(OH)_4^-]$ in seawater.

In many cases $[H^+]$ and $[OH^-]$ are negligibly small compared of concentration of carbonate species. So, in these cases the sum of $[HCO_3^-]$ and $2[CO_3^{2-}]$, determined by an acid titration is referred to as the total alkalinity (A_T) defined as:

$$A_C = [HCO_3^-] + 2[CO_3^{2-}] = b + 2c \quad (26)$$

If water contains Ca^{2+} or Mg^{2+} and carbonate, or it is in contact with calcite, the dissociation equilibrium of calcite affects the carbon chemistry also:

$$CaCO_3 \leftrightarrows Ca^{2+} + CO_3^{2-} \quad (27)$$

where the ions concentrations of $[Ca^{2+}]$ and $[CO_3^{2-}]$ are limited by the solubility of the product.

The principle of alkalinity evaluation describes the following thought experiment, which illustrated by Figure 3.

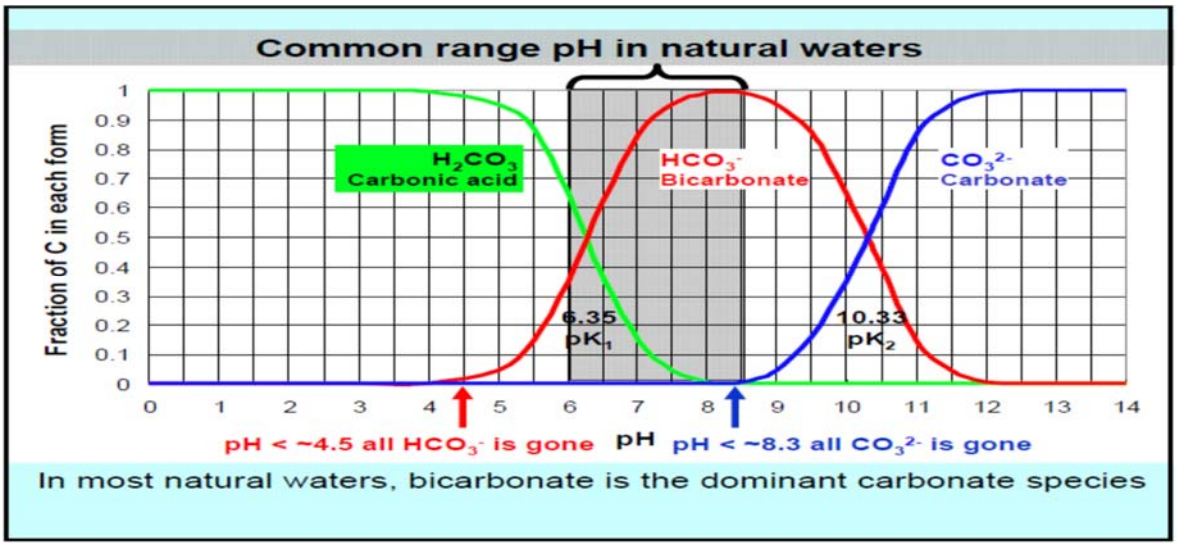

Figure 3: The principle of carbonate containing compounds distribution in water.

First of all, let us assume that *X* moles of solid bicarbonate was added to pure water. Some of dissolved part of this salt would react with protons of water to form H_2CO_3, and some would dissociate to form CO_3^{2-} like shown below:

$$HCO_3^- + H_3O^+ \leftrightarrows H_2CO_3 + H_2O \quad (28)$$

$$HCO_3^- + H_2O \leftrightarrows CO_3^{2-} + H_3O^+ \quad (29)$$

These reactions are written according to the usual convention for acids, as dissociation reactions, but in the particular system under consideration, reaction (29) would proceed in reverse.

The alkalinity is usually expressed as mg/L of $CaCO_3$.
In the case of the equivalent of calcium carbonate, alkalinity expressed as Eq/L.

The equilibrium $\{H^+\}$ of bicarbonate solution obtained, would lie midway between the meaning of equilibrium constants for reactions 28 ($pKa_1 = 10^{-6.35}$) and 29 ($pKa_2 = 10^{-10.33}$). So, equilibrium pH would be 8.3 at this condition (low ionic strength - low solute concentration in water). Being identified in Fig. 3 by blue arrow this pH would correspond to maximal concentration of HCO_3^-. This pH also identified as the point satisfying the balance in the reactions:

$$H_2CO_3 \leftrightarrows H^+ + HCO_3^- \quad (30)$$

$$HCO_3^- + H_2O \leftrightarrows H_2CO_3 + OH^- \quad (31)$$

If the same *X* moles of Na_2CO_3 (instead of $NaHCO_3$) were added to water, some of the carbonate ions would react with protons to form bicarbonate (Reaction 29 in reverse), and this consumption of protons would raise the pH value. The resultant pH would lie at the point where Equation (32) is valid:

$$CO_{3Total} = [CO_3^{2-}] + [HCO_3^-] + [H_2CO_3] \quad (32)$$

This pH identified in Figure 3 as pH CO_3^{2-} (approx. pH 10.5 and higher) and satisfies the proton condition when H_2O and CO_3^{-2} make up the balance:

$$2[H_2CO_3] + [HCO_3^-] + [H^+] = [OH^-]. \quad (33)$$

Similarly, pH CO_2 defined as the pH of a solution in which X moles of CO_2 dissolved. This pH is approximately 4.7. (Note that the exact pH values depend on the concentration X of CO_2 in water.).

In this explanation, all categories of carbonate alkalinity defined in terms of three pH values (pH CO_3^{2-}, pH HCO_3^-, pH CO_2).

In such a way:

Total alkalinity defined as the amount of acid required reduce the pH of studied water to pH of dissolved CO_2; i.e. the amount of acid required to convert of all bicarbonate and carbonate ions into H_2CO_3.

Carbonate alkalinity is the amount of strong acid required to lower the pH of a sample to pH HCO_3^-. At this point the carbonate is converted to bicarbonate, and at lower pH it would be converted to H_2CO_3.

Caustic alkalinity is the amount of strong acid required to lower the pH of a sample to pH $CO_3^{-2.}$ Such alkalinity must result from bases stronger than CO_3^{2-}.

Similarly, the categories of acidity may defined as:

Mineral acidity is the amount of strong base required to raise the pH of a sample to pH CO_2 (stronger acids than H_2CO_3 must be present);

Carbon dioxide acidity is the amount of strong base required to raise the pH of a sample to pH HCO_3^-.

Total acidity is the amount of strong base required to raise the pH of a sample to pH CO_3^{2-}.

To evaluate constituent parts of alkalinity stipulated by OH^-,CO_3^{2-}, HCO_3^-, is recommended to use the Table 1.

Table 1: Alkalinity Relationships.

Volume of titrant required to reach pH=8.3 (P) and pH=4.5 (T) endpoints	Alkalinity due to:		
	OH^-	CO_3^{2-}	HCO_3^-
P=0	0	0	T
P<1/2T	0	2P	T-2P
P=1/2T	0	2P	0
P>1/2T	2P-T	2(T-P)	0
P=T	T	0	0

In this table: P- phenolphthalein alkalinity (pH = 8,3); T- total alkalinity (pH = 4,5).

- If P = 0 (volume of titrant to reach phenolphthalein endpoint equal to zero) the alkalinity due to hydroxyl and carbonate ions is equal to 0. In this case the alkalinity due to bicarbonate ion is equal to the total alkalinity (T).
- If P <1/2 of T, the alkalinity due to hydroxyl ions is 0. In this case the alkalinity due to carbonate ions is 2P. And alkalinity due to bicarbonate ions is equal to the total alkalinity minus 2 times phenolphthalein alkalinity, i.e. T-2P.
- If P = 1/2T than the alkalinity due to hydroxyl ions is 0. The alkalinity due to carbonate ions is 2P. And alkalinity due to bicarbonate ions is equal to 0.
- If P > 1/2T than the alkalinity due to hydroxyl and carbonate ions is 2P. The alkalinity due to bicarbonate ions is equal to 0.
- If P = T than the alkalinity due to hydroxyl ions is equal to total alkalinity (T). In this case the alkalinity due to bicarbonate ions and carbonate ions is 0.

Equipment and reagents

Equipment

- Calibrated pH meter
- Stirring plate;
- Micro magnetic stir bar;
- Clean polyethylene bottles
- Burette with Burette stand and porcelain tittle;
- Volumetric pipets with elongated tips;
- Pipette bulb, or Pipette pump;
- Syringe equipped with a filter holder and a fine-pore filter;
- Conical flask (Erlenmeyer flask);
- 250 ml measuring syringe;
- Standard flask;
- Wash bottle;
- Beakers.

Chemicals required

- Standard sulfuric acid 0.02M;
- Phenolphthalein;
- Sodium thiosulfate 0,01M;
- Activated carbon;
- Methyl orange (or Bromocresol green);
- Distilled water.

Tasks performance order

- You should get the samples of water from original sources. If this is not possible, the artificially prepared solutions can used.
- Appropriate samples should include river or lake water, groundwater (if possible from a well, and if not, a sample of bottled mineral water—preferably from a natural source), seawater (if not available, it can be prepared synthetically or obtained from a commercial source).

- The samples must be collected in clean polyethylene bottles, and analyzed as soon as possible after sampling. Otherwise, the values may vary substantially.
- Estimated time required to complete the experiment depends on the number of samples analyzed (approx. 5–20 min per sample per analysis). All experiments may carried out in one or two sessions.
- Experimental part consists of measures the pH, alkalinity and buffering capacity of water samples and compares the values among them as well as with those of tap and distilled or deionized water. The alkalinity will be measured by titration with dilute sulfuric acid up to two specific pH values: 8.3; and 4,5 and by obtaining of titration curves using pH meter. This will make possible to calculate the different contributions of species responsible for the alkalinity and evaluate the buffering capacity of water samples. The acid–base indicator phenolphthalein is used to indicate the pH = 8.3 endpoint and to obtain the P-alkalinity. Results can best interpreted in the light of algorithm described in Table 1.To identify the amount of acid required to reach the 4,5 endpoint, methyl orange or bromocresol green indicators should be used.
- The total amount of acid required to reach endpoint 4.5 indicates total alkalinity. For a more accurate titration, the pH searching must followed with a pH meter. Buffering capacity of water samples evaluated as quantity of acid required for shifting pH of one liter of studied water to one unit of pH.
- You will compare the amount of titrant added and the pH of each sample, determining the alkalinity and buffering capacity.

Safety Measures

The titrants should not come in contact with the skin or eyes because they may be corrosive. You must consider all the safety measures normally taken when handling this kind of reactants. In case of spillage of an acid solution or of skin contact, wipe clean with a clean cloth and wash thoroughly and abundantly with water (sprinkle the table or surface with sodium bicarbonate). All of the residues generated in this experiment can be disposed of down the drain once they have been neutralized.

Sampling and titration

1. Collect samples (or prepare them synthetically) of: (1) river or lake water, (2) ocean water, (3) mineral water (or if available, use groundwater), (4) tap water, and (5) deionized water.

If automatic titration equipment is available, use them, otherwise use a calibrated pH meter throughout the entire experiment and wait until stable readings obtained.

2. Measure the pH and temperature of each sample. If the pH is above 8.3, determine the P-alkalinity. If it is not, only the T-alkalinity (i.e., methyl orange or bromocresol green alkalinity at pH = 4.3).

3. To prevent masking of the endpoint when using colored indicators, make sure the sample is colorless and free of turbidity. To have this condition, filter the sample prior to titration and if the color were a problem, add a small amount of activated carbon (prior to filtration). Filtration can be done by means of a syringe equipped with a filter holder and a fine-pore filter. To

eliminate any free chlorine that might interfere with the titration, add a drop or two of 0.01M sodium thiosulfate.

4. Place burette in a stand, rinse it with a small amount of the acid titrant, and fill it to the desired mark.

5. With a volumetric pipet, take a 10-mL portion of the water sample and place it in a 25- or 50-mL beaker. Place a micro magnetic stir bar inside the beaker and put the beaker on a stirring plate. Immerse the bulb of the pH electrode in the liquid sample, without touching the stir bar. Measure the pH.

6. Add 2 to 3 drops of the phenolphthalein indicator (e.g., with a Beral pipet). Observe if any color appears.

7. If upon adding the P indicator there is no color, then the P-alkalinity is zero. In this case, immediately add 1 to 2 drops of the methyl orange (or of the bromocresol green) indicator and start titrating to the endpoint.

8. If a pink color appears upon adding the phenolphthalein indicator, titrate drop wise (in 0.1 or 0.2 mL increments), stir gently, and record the resulting pH and volume of titrant added. Note the pH reading at the point when the color of the indicator disappears (it must be close to 8.3). Then, immediately add 2 to 3 drops of the methyl orange (or the bromocresol green) indicator, and continue the titration until the exact 4.5 endpoint is reached (the solution turns Salmon in the case of methyl orange or yellowish in color, in the case of the bromocresol green indicator).

9. Repeat the same technique for each water sample.

To get titration curves you will caryfully add drops of standard acid to various samples and record the resultant pH values. The data that you obtain will look similar to that shown in Figure 4 There are regions where the pH changes rapidly with each acid addition, and regions where the response is much less.

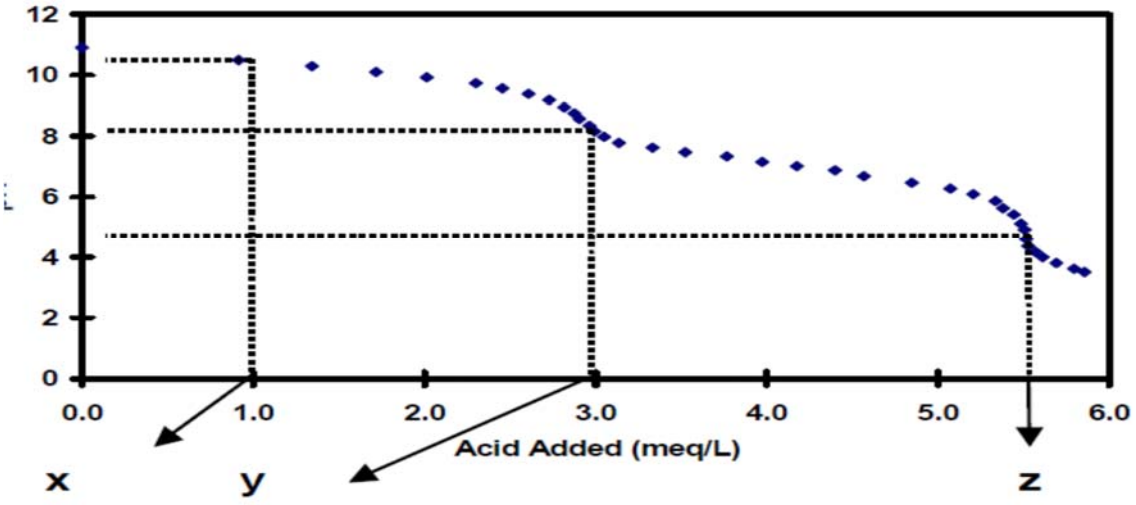

Figure 4: Titration curve. Endpoints of the titration are shown in the plot (point z for total alkalinity, point y for carbonate alkalinity, point x for caustic alkalinity).

You can determine from this titration curve the approximate endpoints (x, y, z) for the various alkalinity species (see discussion above).

LABORATORY REPORT

Alkalinity and Buffering Capacity of Water

Name _____Section_____ Date_____

Instructor_____ Partner_____

Experimental Tittle:_____

Objectives_____

Flow sheet of procedure_____

Waste containment procedure_____

PART “A” DETERMINATION OF ALKALINITY

Origin of samples:

№1_____

№2_____

№3_____

№4_____

№5_____

Visible characteristics of the sample (color, odor, suspended solids present, etc.)

№1_____

№2_____

№3_____

№4_____

№5_____

Precautions observed during the sampling. Sampling procedure for each sample:

№1_____

№2_____

№3_____

№4_____

№5_____

EXPERIMENTAL DATA

1) Initial pH of the samples:

№1_____

№2_____

№3_____

№4 Tap water_____

№5 Deionized water_____

Analysis of obtained results

1. From the experimental data obtained with each sample tested, report the alkalinity values and the concentration of each alkalinity species as mg/L of $CaCO_3$.

To calculate the alkalinity, apply the following formula:

$$\text{Alkalinity (mg } CaCO_3\text{/L)} = \frac{(V\ \text{acid,mL})\ (\text{M,acid solution})(50\ \text{g/aquivalent CaCO3})\ (1000\ \text{mg/g})}{(V\ \text{of sample,mL})}$$

Fill the table 2 of Report.

Table 2: Alkalinity structure of studied samples.

Sample	P-Alkalinity as $CaCO_3$	M- Alkalinity as $CaCO_3$	Total Alkalinity as $CaCO_3$
№1			
№2			
№3			
№4			
№5			

To determine the approximate concentration of hydroxide, carbonate and bicarbonate ions in each sample use the algorithm described in Table 1 of theoretical part.

The dominant species at pH = 4.5 are assumed to be bicarbonate and carbonate, and when OH− ions are present, no bicarbonate ions can be present. It is also assumed that [H+] is not relevant in alkaline pH values, and that one half of the carbonate ions present become neutralized at the pH = 8.3 endpoint. Fill the table below based on the results of titrations performed by you.

Alkalinity Relationships.

Volume of titrant required to reach pH=8.3 (P) and pH=4.5 (T) endpoints	Alkalinity due to:					
	OH^-		CO_3^{2-}		HCO_3^-	
P=0	0		0		T	
P<1/2T	0		2P		T-2P	
P=1/2T	0		2P		0	
P>1/2T	2P-T		2(T-P)		0	
P=T	T		0		0	

Carry out titration with using of pH meter

Plot the titration curves of different water samples and designate the points of pKa and titration endpoints

The titration data should be assembled in separate table like shown below and after that plotted as pH (y-axis) vs. acid added (x-axis) curves for different studied samples of water.

Table 3: Example titration data of 50 mL natural water containing carbonate species. The titrant is 0,01 M H_2SO_4.

Acid added (mL)	pH		Acid added (mL)	pH		Acid added (mL)	pH
0	10.9		8.8	8.16		18.2	5.86
2.4	10.49		9.0	7.98		18.4	5.62
3.6	10.29		9.3	7.78		18.7	5.41
4.7	10.10		10.0	7.62		18.9	5.11
5.6	9.92		10.7	7.47		19.0	4.91
6.5	9.73		11.6	7.33		19.05	4.59
7.0	9.56		12.4	7.15		19.1	4.36
7.5	9.38		13.2	7.01		19.3	4.17
7.9	9.18		14.1	6.87		19.5	3.99
8.2	8.95		14.8	6.68		19.9	3.80
8.4	8.75		16.0	6.46		20.4	3.61
8.5	8.57		17.0	6.27		20.7	3.50
8.7	8.34		17.6	6.09			

Table 4: Titration data of 50 mL(100mL) sample of_____ (natural water , seawater, tap water, mineral water) containing carbonate species. The titrant is 0,02 M H_2SO_4.

Acid added(mL)	pH		Acid added (mL)	pH		Acid added(mL)	pH

Prepare the plots of pH (y-axis) vs. acid added (x-axis) for different studied samples of water (natural water , seawater, tap water, mineral water) containing carbonate species like shown in Figure 5.

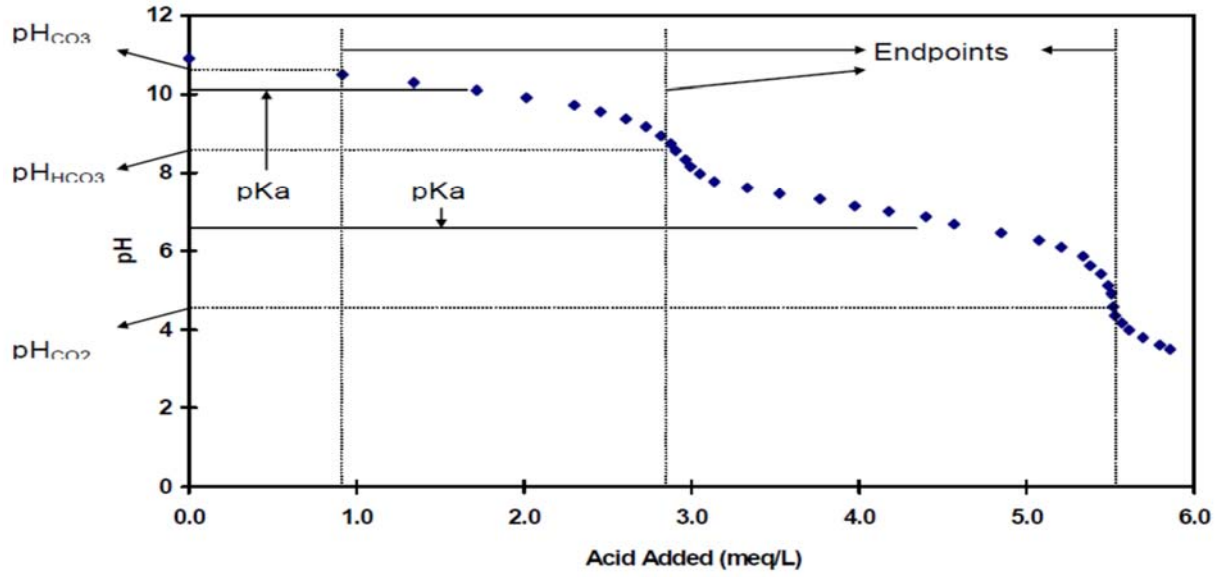

Figure 5: Example of plotting titration curve and designation of inflection points on it.

The inflection points on the titration curve correspond to the pK_a for the carbonate system (equivalence points are 6.35 and 10.33 consequently) and the equivalence points (pH CO_3^{2-}, pH HCO_3^- and pH CO_2).

- Compare the titration curves obtained on different water samples.
- Explain why the resulting curves have a different shape.
- Calculate the buffering capacity of different water samples using titration plots.
- Collect the results obtained in the table 5 like shown below

Table 5: Buffering capacity of different water samples at chosen pH values**.**

Sample	pH range	Buffering capacity(M of acid added per unit of pH in 1L of water sample)
№1		
№2		
№3		
№4		
№5		

Report content

1. In the Introduction you should explain global importance of carbonate system and why water`s alkalinity is of interest t why the alkalinity of water is of interest to specialists from different fields of knowledge.

2. In the Results section, insert the tables and figures described under headings: Origin of samples, Visible characteristics of the samples (color, odor, suspended solids present, etc.), Precautions observed during the sampling, Initial pH values of samples, Alkalinity measurement data obtained by titration up to chosen endpoints (without using of pH meter), Titration curves and results of there analysis

Explain the differences of obtained results related to different samples of water. Why your measured values for alkalinity components are different in different samples? What effect does atmospheric CO_2 have on the alkalinity and the carbonate species distribution in water samples? Present tables listing the alkalinity structure for all the samples that you measured. Discuss and compare these results and discuss whether any of these samples would be susceptible to acidification from acid rain. Evaluate whether there is a relationship between alkalinity and pH. Discuss the results of buffering capacity measurement.

Discussion issues:

1. Why the distilled water or DI water considered to have no alkalinity and buffering capacity?

2. Why the sample of seawater exhibit high alkalinity and buffering capacity?

3. What is the reason of surface water buffering capacity?

Test yourself with answers to the following questions:

1. The alkalinity of water is an indication of:
    a) Base neutralizing capacity;
    b) Acid neutralizing capacity;
    c) Quantity of base present;
    d) Quality of base present.
2. Alkalinity is present due to all except:
    a) Bromates;
    b) Phosphates;
    c) Silicates;
    d) Chlorides.
3,Alkalinuity is not caused by:
    a) Carbonate ions;
    b) Bicarbonate ions;
    c) Hydroxyl ions;
    d) Chloride ions.
4.The phenolphtalein alkalinity is present then the pH of that water will be more than:
    a) 8.3;
    b) 9.3;
    c) 7.3;
    d) 6.3.
5.Alkalinity of natural water is manly due to presence of:
    a) Bicarbonates;
    b) Bromates;
    c) Phosphates;
    d) Silicates.
6.The bicarbonate equivalence point of rain water normally occur at pH:
    a) 2.5;
    b) 3.5;
    c) 4.5;
    d) 5.5.
7.What is ppm?
    a) Parts per meter square'
    b) Parts per meter'
    c) Parts per million'
    d) Parts per millimeter.
8.The normality of acid used in the titration is:
    a) 0.2N;
    b) 0.02N;
    c) 0.002N;
    d) 2.0N.
9.A standard solution is a:
    a) Solution of accurately known strength;
    b) Solution of accurately known pH;
    c) Colored solution;
    d) Colorless solution.

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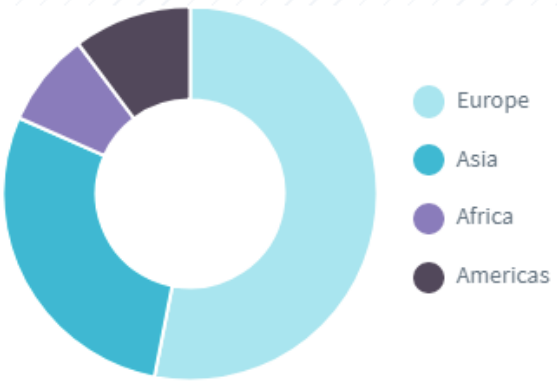
45 Universities across 30 nations, since 2012. A distribution chart illustrating the diverse opportunities available through the Water Harmony network.



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