Ministry of Higher Education and Scientific Research
DJILLALI LIABES University, Sidi Bel Abbes
Faculty of Technology

Polycopy « Physicochemical and biological treatment of wastewater»

(Practical work)

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Foreword

The objectives of thishandbook are to introducestudents in the Master's program in Environmental Process Engineering and Process Engineering to the theoreticalknowledgeacquired in the Physicochemical and BiologicalTreatment of Wastewater course (wastewater purification).

Studentswillbe able to use bench-top measuringequipment, as well as pilots and software, to carry out water purification studies.

The content of this module enables students to understand the fundamentals of biologicalwastewatertreatment, and to design the variouswastewatertreatment plants intended for urban or industrial settings.

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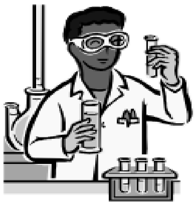
TP01 :
DETERMINATION OF CHEMICAL OXYGEN DEMAND (COD)

DJILLALI LIABES- SIDI BEL ABBES UNIVERSITY.
FACULTY OF TECHNOLOGY
DEPARTMENT OF ENERGY AND PROCESS ENGINEERING

MASTER 2: ENVIRONMENTAL PROCESS ENGINEERING
TP: PHYSICO-CHEMICAL AND BIOLOGICAL TREATMENT OF WASTEWATER



TP N 01 :
DETERMINATION OF CHEMICAL OXYGEN DEMAND (COD)
Standard NF T90-101 (0-1000mgO2/L)

- **INTRODUCTION :**

As they break down, organicmatter consumes the oxygendissolved in water. If tooabundant, they can cause excessive oxygenconsumption, resulting in asphyxiation of aquaticorganisms. Chemical oxygendemand (COD) is a measure of the concentration of organic or mineralmatter, dissolved or suspended in water, in terms of the quantity of oxygenrequired for its total chemicaloxidation. By measuring COD, we can assess the organicmatterload of wastewaterbefore and afterphysical, chemical or biologicaltreatment, in order to monitor the operation of a WWTP and the activity of micro-organisms, makingit an indicator of the degree of pollution.

Chemical OxygenDemand (COD):is the mass concentration, expressed in mg/L, of oxygen (O_2), equivalent to the quantity of potassium dichromate ($K_2Cr_2O_7$) consumed by the oxidizablematter in the solution.

- PRINCIPLE:

- COD determination comprises 02 steps:
  - ✓ Stage1:chemicaloxidation of the reducingorganicmattercontained in the water, by an excess of potassium dichromate $K_2Cr_2O_7$.This is a so-called indirect determination.
- This oxidationiscarried out in a sulfuric medium, in the presence of Ag_2SO_4 and $HgSO_4$, boiling at reflux (gentle) for 1.5 hours in a flaskfittedwith a cooler.
  - ✓ Step2:Aftercooling, measureexcess $K_2Cr_2O_7$with MOHR salt.

- PURPOSE:

- Determine the Chemical OxygenDemand (COD in mg/L) of a water sample.

- MATERIALS, MEASURING EQUIPMENT AND PRODUCTS :

Measuringequipment	Products
- Graduated burette - Graduated pipette + pro-pipette - 100ml, 250ml volumetricflasks. - 250 ml beaker. - Stirrer + magnetic bar. - Thermometer or electro-metric probe. ➢ *Arrangement of a reflux heating system :*	- Sample water - Potassium dichromate ($K_2Cr_2O_7$ at 0.04M) M=294 g/mol - MOHR salt $[(NH_4)_2Fe(SO_4)_2.\ 6H_2O]$ at C_2 concentration (approx. 0.12M)M=392g/mol - Mercury sulfate ($HgSO_4$) - Silver sulfate (Ag_2SO_4)at 10g/L - H_2SO_4 at C=4M.

- Flat-bottomedground-glass flask (150 or 250ml) + stopper. - Ball or serpentine refrigerant - Flexible hoses for water inlet and outlet - Balloonheater - Elevating support. - Stand for suspendingflask and coolant	- Pumice stones or boilingregulatorbeads - Ferroin (ferrousorthophenantroline - colorindicator) - Ice bath - Distilled water.

- HANDLING (Operating mode) :

Beforetaking the test sample, the water sample must becarefullyhomogenized by shaking the bottle, and if the water sample has been takenfrom the inlet of a wastewatertreatment plant, itispreferable to diluteit 2 to 5 times (to avoid the riskthat the dose of K2Cr2O7 introducedinto the water to beanalyzedistoolow, and thatitisentirelyreduced by the sample, and without an excess of K2Cr2O7 at the end of the reaction, the measurementis impossible).

➢ Stage 1:oxidation of organicmatter in water.

- Dans un ballon à fond plat muni d'un bouchon, introduire :
- **V_0= 10ml** précisément d'eau à analyser (effluent).
- **5ml** de$K_2Cr_2O_7$ à **C_1 =0.04M** contenant 0.4 g de $HgSO_4$.
- **Ajouter 05 à 06 billes régulatrice d'ébullition (ou pierre ponces),** boucher et homogénéiser en agitant doucement.

1-Using a pipette, slowly and carefullyadd 15ml (H2SO4(4M) + Ag2SO4 (10g/L)) in a fume hood. Shake the flaskcircularly and cool in an ice bath.
2- Place the flask in itsheating support (flaskheater).
3- Place the cooler (ball or coil) on top of the flask and supplyitwithtap water.
4- Start heating at gentleboiling for 1h:30.
Réaliser part-3 duringheating.
5-After 1h:30, switch off the heater.
6-Allow to cool for a few minutes, thenwash the insidewall of the coolerwithdistilled water, carefullypouring about 75 ml of distilled water through the top of the cooler.
7-Remove the flaskfrom the heater and cooler, then cap the flask.
8- Transfer the contents of the flask to a 250ml Erlenmeyer flask, rinsing the flaskwith a minimum of distilled water and adding the wash water to the mixture.
9-Nowproceed to step 2.

➔NB :performing a blank test (in parallel)
- Follow the samesteps as in step-1, except use 10ml (V0) of distilled water instead of the water sample (effluent).

✓ Step2: Dose excessoxidantwith MOHR salt (Reducer).

➔NB :This stepapplies to both the sample to beanalyzed and the blank test.
- Introduceinto the Erlenmeyer flaskrecoveredfromstep1:
- A few drops of ferroine (coloredindicator for redox assays).
- Introduce the magneticrod
1- Fill the burette with MOHR salt solution at C2 (assayed in step-3).
2- Start the colorimetricdetermination of the excessoxidizing agent (K2Cr2O7,C1) with the reducing MOHR salt solution, pouring drop by drop until the color changes (bleu□rouge).
3- Note the volume at equivalence (color change) **Ve** and **V_B** (equivalent volume to measureorganicmatter in the blank test).

✓ **Step3: Calibration of MOHR saltreducing solution.**

As this solution (MOHR salt) isunstable over time, itsmolar concentration needs to becheckedregularly, using an acidified (K2Cr2O7,C1) solution.
1- Introduceinto an Erlenmeyer flask or beaker :
- Vox= 10ml of a solution of K2Cr2O7 at Cox=C1= 0.04M.
- In the fume hood, using a pipette, slowly and carefullyadd 15ml (VH2SO4) of H2SO4 (4M), shaking the Erlenmeyer circularly and coolingit in an ice bath.
- Add a few drops of indicator solution (ferroine).
- Attach a magneticstirring bar and switch on the magneticstirrer.
2- Fill burette with MOHR saltreducing solution.
3- Dose thisreducing solution at C2.
4- Note the equivalence volume V2 responsible for the color change fromgreen-bleu□rouge to brown.
5- Calculate the C2 concentration value by applying the followingexpression:

$$\mathbf{C_2\ (en\ M)=[Fe^{2+}]=6C_{ox}\ .\ V_{ox}/V_2}$$

- **QUESTIONS :**

I) Dosingoperation (steps 1 and 2).

1-Write the ½ Redox equationsrelating to eachreagent.
The following couples are given:$\mathbf{Cr_2O_7^{-2}/Cr^{3+};\ Fe^{2+}/Fe^{3+}}$**.**

2- Deduce the balance reaction (reaction -1) of the colorimetricassay.
3- Complete the followingprogress table and determine the following expression between the 02 reagents: $n_{ox}=\dfrac{C_2.V_e}{6}$.

States	Progress	…..$\mathbf{Cr_2O_7^{-2}}$+ …… $\mathbf{Fe^{2+}}$ + …...$\mathbf{H^+}$➔$\mathbf{2Cr^{3+}}$+…..$\mathbf{Fe^{3+}}$+…..$\mathbf{H_2O}$					
S. initial	x=0	$\mathbf{n_{ox}}$ **inexcess in the balloon**	$\mathbf{n_{red}}$ **toachieveequivalence**	excess	0	0	excess
S. Final (Equivalence)	x_f= x_{eq}	$\mathbf{n^f_{(ox)}}$**=**.............	$\mathbf{n^f_{(red)}}$**=**.............	excess	2 x_{eq}	6 x_{eq}	excess

4- The total quantity of dichromate ions $\mathbf{n_T}$introducedinto the flaskbeforeheatingwas put intoexcess: a certain quantity of these ions **(noted$\mathbf{n_{MO}}$)**reacted by oxidizing the organicmatter, the other part, the excess**($\mathbf{n_{ox}=n_{excess}}$)**wasdosed by the MOHR salt solution.

- With the help of the diagramgiven in the PRINCIPLE of the practicalwork, and knowingthat :$\mathbf{n_T=n_{MO}+n_{ox}}$**,** retrouver la relation suivante : $n_{MO}=C_1.V_1-\dfrac{C_2.V_e}{6}$.

- **II) Oxidation of organicmatter (OM) and oxygenequivalence :**

  The dichromate ions notednMO, whichwill enable the oxidation of organicmatter, will first reactwith water H2O to formoxygen O2.

  1- Write the ½ Redox equations for the pairs to which the water and dichromate ions belong. Data**:**$\mathbf{Cr_2O_7^{-2}/Cr^{3+}\ ;\ O_2/H_2O}$**.**

  2- Determine the balance reaction**(reaction -2)**.

  It isassumedthat the O_2formed in the previousreactionwillsubsequentlyoxidize the organicmatter in the water, enabling the COD to bedetermined.

  3- According to reaction-2, wehave:**1mol ion**$\mathbf{Cr_2O_7^{-2}}$**➔ 3/2 moles of** $\mathbf{O_2}$ **formed.**

- Finding the relationshipfor $\mathbf{n_{MO}}$ and $\mathbf{n_{O2}}$**.**
- **III) Determination of « DCO »:**

1- From the previousresults in parts I) and II), show the followingliteral expression :

$$n_{O_2} = \frac{3}{2}.(C_1.V_1 - \frac{C_2.V_e}{6})$$

Determine the expression for the effective molar concentration **(in mol/L) [O_2]**, then the mass concentration **$t_{m(O2)}$ (g/L)** in equivalentoxygen, for a volume of water sample**V_0**analyzed.

NB :*In order to takeintoaccount the blank test, itisnecessary to make the following correction beforecalculation:* $V_1 = \frac{V_B.C_2}{6.C_1}$ avec C_1= $[Cr_2O_7^{-2}]$= 0.04M

2- Show the followingliteral expression for COD (mg O_2/L):

$$DCO(mg d'O_2 / L) = \frac{8000.C_2(V_B - V_e)}{V_0}$$

3- Calculate the COD value of the water sampleanalyzed.

4- Knowingthat**the standard sets the COD limit at 120mg/L**. for water discharged by the farmaftertreatment.

- Are the results in line with the standard?

Water qualityisclassifiedaccording to the following quantitative criteria:

0.5< DCO <5 mg/L	**drinking water**
8< DCO <100 mg/L	**purified water (non-potable)**
800 < DCO < 1200 mg/L	**domesticwastewater**
1500 < DCO < 10000 mg/L	**industrialwastewater**

- From the table above:deduce the quality of your analyzed water sample.

TP02 :

DETERMINATION OF BIOCHEMICAL OXYGEN DEMAND (BOD_5)

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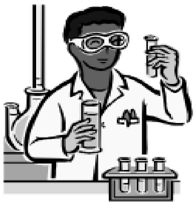


TP N 02 :
DETERMINATION OF BIOCHEMICAL OXYGEN DEMAND (BOD_5)

- INTRODUCTION :

BOD, or BiochemicalOxygenDemand, corresponds to the quantity of oxygenrequired by aerobicmicro-organisms in water to oxidizeorganicmatterdissolved or suspended in the water. It thereforerepresents the potentialconsumption of oxygen by biologicalmeans. This parameteris a good indicator of a water'sbiodegradableorganicmatter content (anypollutingbiodegradableorganicmatter leads to oxygenconsumption) during self-purification processes.

BOD isused to measure the quality of water in a jar (surface water:rivers, lakes..., wastewater: treatment plants, industrial effluents...). The water analyzedcontains a quantity of biodegradableorganicmatterwhich, whenreleasedinto the naturalenvironment, willbebiologicallydegraded, leading to the development of aerobicmicro-organisms. This proliferation causes a drop in dissolvedoxygen in the receivingenvironment, leading to asphyxiation of the speciespresent. This analysistherefore enables us to assess the impact of the discharge on the receivingenvironment.

Biochemicaloxygendemand (BOD) is the quantity of oxygenrequired to oxidize (biodegrade) organicmatter by biologicalmeans (oxidation of biodegradableorganicmatter by bacteria).

It isused to assess the biodegradable fraction of the carbonaceouspollutantload in wastewater.

- PRINCIPLE :

BOD ismeasuredafter 5 days (=BOD5), at 20°C (atemperature favorable to the activity of O_2-consuming micro-organisms) and in the dark (to avoidparasiticphotosynthesis). Twosamples are required: the first to measure the initial O_2 concentration, the second to measure the residual O_2 concentration after 5 days. $BOD_5$is the differencebetweenthese 2 concentrations. Measurements are taken on the same volume, and the second sampleiskept for 5 days in the dark at 20°C.

- PURPOSE :

- Determine the BiochemicalOxygenDemand in a water sample to beanalyzed by 02 methods:

- ✓ Manometricmethod (respirometry) based on the principle of the WARBURG respirometer, in which a depression (decrease) in O2 isdirectlyrecorded by a device (a volume of sampleisplaced in ground-glass flasks).

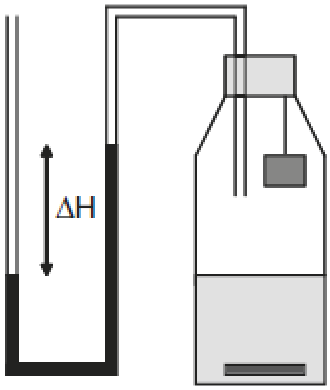
- ✓ Dilution method.

- MATERIALS, MEASURING EQUIPMENT AND PRODUCTS:

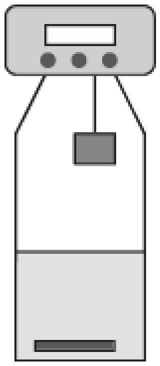
Materials, Measuringequipment	Products
- Graduated pipette + pro-pipette - 100ml, 250ml volumetricflasks. - 500 ml beaker. - Stirrer + magnetic bar. - Thermometer or electro-metric probe. *<u>Oxitop® BOD meterdevices:</u>* - 02 to 06 brownbottles. - Oxitopheads. - Rubber cups. - Gaugedoverflowflasks. - 20°C air-conditioned cabinet + agitator.	- Sample water (industrial effluent) - Distilled water. - NaOH pellets, KOH or sodated lime. - N-allyl-thiourea ($C_2H_8N_2S$).

- Diagram of a manometricmeasuringdevice :

There are 02 types of equipment on the market (seediagramsbelow).
The oldestdevicesfeature a manometric tube whichisused to determine the vacuum corresponding to O_2consumption. Newerdevices use a cap fittedwith a pressure sensor (OxiTophead) whichautomatically stores pressures at times 1, 2, 3, 4 and 5 days.
In all cases, the incubation flaskisequippedwith a shaking system and a podcontaining KOH, which traps the carbondioxidereleasedduring the biodegradation of oxidizable (reducing)organicmatter.



1re génération



2e génération

- HANDLING (Operating mode) :

1- Rinse the brownbottlewith the sample (domestic or industrialwastewater) to bemeasured. Drain well.
2- Homogenize the sample by shaking and aeratingit to saturateitwithdissolved air.
3- Start a measurement cycle by performing the followingsteps:

a) Place in the bottles the volume of sample (effluent:domestic or industrialwastewater) determined on the basis of the scale to beused, measuredwith a graduatedcylinder.

b) Place a magneticanchor (bar magnet) in eachbottle.

c) Place sufficientabsorbers (causticpotash KOH in flakes or soda lime (CaO 65-80%+NaOH 5-20%+H_2O 6-18%(w/w)) in the alkali container or pod of eachbottle to fillitwithoutholesappearing on the sides.

NB :*If any of the absorber fallsinto the bottle, washitthoroughlybeforeinserting the sample to beexamined.*

a) Place the bottles in theirhousings in the unit, screwing the caps on withoutclosingthemhermetically.

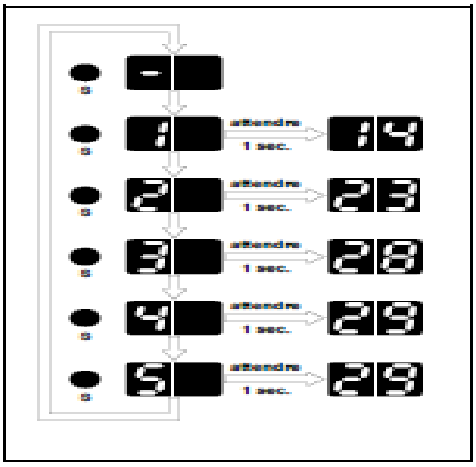
b) Place the unit in the thermostaticcoolingchamber, set at the chosentemperature (20°C), to determine the D.B.O. Connect the magneticstirring system to the electrical power supply by pluggingitinto the socket (constant stirring). Activate the InnerSupply switch on the front panel of the thermostaticcooler.

c) After approx. 30-40 minutes, the instrument and samplesshouldbe in thermal equilibrium at the selectedtemperature.

d) Place and screw the D.B.O. Sensor onto the bottles. Reset eachmeasuring point (press and hold 02 buttons "M" and "S" simultaneously, to clearanyresidual memory), select the appropriatescale and restart the measuringcycle.La mesure va démarrer dès que la tête mesurera une température de 20 °C.

- The oxitopwillautomatically record a value every 24 hours, for 5 days.
- Duringthis time, to view the current value, press the "M" key (the key thatinformsyou of the measurementscale).

4- After the 05 days, readeach value by pressing the **"S"** key as follows :



5- Expression of results :

BOD_5 mgO_2/L = reading in the OxiTophead x conversion factor of BOD.

- **QUESTIONS :**

1- Whatis the role of adding KOH or soda lime granules, if not NaOH?

2- In some cases of BOD measurement, a few pinches of allylthiourea (C2H8N2S) are initiallyadded to the brownbottle. Why or whynot?

3- Fill in the following table with the results of yourmeasurements :

Type of water to beexamined	**Quantity of O_2 (mg/L) measureddaily by OXITOP at T=20°C**					
	Au départ (0h)	**1st day (24h)**	**2nd day (48h)**	**3rd jour (72h)**	**4th day (96h)**	**5th day (120h)**
Domestic wastewater (sewage)						
Industrialwastewater						
Water …………..						

4-Draw the curve:**Q_{O2} (in mg/L)=f(time)**. (eitherwith**Regressi®** software or on millimetricpaper). Comment.

5-Using the table in the APPENDIX, determine the BOD_5 value for each type of sampleanalyzed.

6-Calculate the **COD/BOD_5** factor for each type of sampleanalyzed. Whatdoesthis ratio represent and whatisitssignificance?

7- Apart from COD, whatotherparameters influence BOD_5?

8-Describe the dilution method (procedure) not used in thislaboratory?

TP03 :

PHYSICO-CHEMICAL CHARACTERIZATION OF WASTEWATER (TSS, Permanganate Index)

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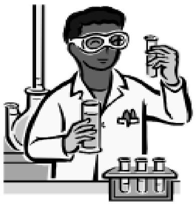

TP N 03:
PHYSICO-CHEMICAL CHARACTERIZATION OF WASTEWATER (TSS, Permanganate Index)

- **INTRODUCTION :**

Organicmatter, present in water and resultingfrom exchanges between the biosphere and the hydrosphere, can be a major source of pollution. While water is essential to life, itisalso one of the main vectors of disease (gastro-enteritis, cholera, malaria...) and itsdecomposition can lead to the asphyxiation of aquaticfauna. Microbiologicalriskis an essential parameter to takeintoaccount. It isthereforenecessary to assessthis pollution and, above all, to reduceit, by analyzing water fromdomestic, agricultural or industrialdischarges (waste) for the following physico-chemical and biologicalparameters:

➔Particulate pollution :
- Suspendedsolids (TSS)

➔Pollution organic :
- Chemical oxygendemand (COD)
- Biochemicaloxygendemand (BOD)
- Permanganate index (PI)

➔Pollution causing eutrophication :
- Total nitrogen (NT)
- Total phosphorus (TP)

➔Pollution bacteriological :
- Bacteria (total and fecalcoliforms, Escherichia colis...etc)
- viruses

- **PURPOSE :**
  - ➢ Determination of the followingparameters:

  - Suspendedsolids**(part 1)**
  - Permanganate index **(part 2)**.

- **MATERIALS, MEASURING EQUIPMENT AND PRODUCTS:**

Materials, Measuringequipment	Products
- Graduated burettes 50ml or 25ml - Graduated pipette + pro-pipette - 1L, 100ml, 250ml volumetricflasks.	- Sample water - Distilled water. - $KMnO_4$ ($2.0.10^{-3}$M).

- Stirrer + magnetic bar. - Thermometer or electro-metric probe. - 1L graduatedcylinder - 900ml, 250ml beakers + Large model funnel - Filterpaper (Wattman GFC-47mm glass microfibres) - Fiberglassfunnel - Vacuum filtration equipment (vacuum flask + vacuum pump or water tube orifice + flexible hose) - *Reflux heating system :* - Flat-bottomedgroundflask (150 or 250ml) + stopper. - Ball or serpentine refrigerant - Flexible hoses for water inlet and outlet - Balloonheater - Elevating support. - Stand for suspendingflask and coolant	- H_2SO_4 at (2M). - Sodium oxalate ($Na_2C_2O_4$ at $5.0.10^{-3}$M). - Pumice stones or boilingregulatorbeads. - Ice bath

- HANDLING (Operating mode) :

- Part 1 :TSS determination.

1-Introduce**300 ml** of sample water into a beaker (note the source or type of water sampled).

2- Carry out the followingsteps:

3-Removecoarseparticlesfrom the sampleusing a 5 mm square meshsieve (AFNOR module no. 38) and, in the presence of fats and oils, homogenize the sievedraw water.

4-Introduceinto a beaker:**V= 500 ml** of sample water (note source or type of water sampled).

5-Take a filterpaper (a GFC membrane) and mark itcarefullyso as not to damage it.

6-Weigh the filterpaper and note its mass m_0 (in mg).

7- Place the filter (or membrane) on the filtration manifold (funnel).

8-Proceedwith filtration, transferring the volume of water collected to the filterpaper.

9-Recover the filterpaper (membrane) after filtration, then place it in an oven at 105°C for **1h30 min** to removeexcess water.

10-Weigh the membrane again, after drying, and record its mass **m1** (in mg).

N.B : the volume filtered must not exceed 1L and filtration must not last more thanhalf an hour

Expression of results:

$$MES(mg/L) = \frac{m_1 - m_0}{V(enL)}$$

Note:Retain water from filtration or centrifugation operations for determination of solids in solution.

➢ Part 2 :permanganate index determination(IP).

The permanganate index of water corresponds to the mass of oxygen "O_2" consumed by the oxidizableorganicmattercontainedin 1.0 L of water. It isexpressed in milligrams per liter.

- **Step1:** A sample of water isoxidized in an acid medium, for 10 minutes at boiling point, by a solution of potassium permanganate in excess.

- Step2:Anyremaining permanganate ions are reactedwith an excess solution of ammonium oxalate.
- **Step3:** All remaining oxalate ions are reactedwith the minimum volume of potassium permanganate solution.

- **HANDLING (Operating mode):**

Step1 :

- Introduce$V_{éch}$ = 25.0 mL of the water studied, a bar magnet and 5.0 mLsulfuricacid (2 mol.L^{-1}) into a flask.

- Introduce a volume V_1 = 20.0 mL of a potassium permanganate solution S_1 (K^+(aq) , MnO_4^-(aq)) of concentration C_1 = 2.0.10^{-3} mol.L^{-1}into the pouringfunnel.

- Set up the water coolervertically, with the pouring ampoule on itsside. Start water circulation, agitation and heating (thermostat set to maximum). Pour in potassium permanganate solution when mixture begins to boil.

- Bring to a gentleboil (usingpumice stones) for 10 minutes.

Step2 :

- Remove the ampoule and pipette in a volume V_2 = 20.0 mL of sodium oxalate solution S_2 (2 Na^+(aq) , $C_2O_4^{2-}$(aq)), concentration C_2 = 5.0.10^{-3} mol.L^{-1}.

Step3 :

- When the solution isdiscolored, stop the water flow and pour the contents of the flaskinto an Erlenmeyer flaskwhile the mixture (titrated solution) isstill hot. Fill the graduated burette with solution S_1 .
- Place the Erlenmeyer on the magneticstirrer and start titratingyour mixture whileslowlypouring in solution S_1. Stop adding solution when the pink tint persists for more than 30 seconds.
- Then record the volume $\mathbf{V_{E1}}$ of solution S_1poured in as the equivalent volume (volume for which permanganate and oxalate ions are completelyconsumed).

➔**NB :blank test (in parallel)**

- **Follow the sameprocedure as in the previousthreesteps, but use 25ml of distilled water instead of the water sample (effluent).**

- **QUESTIONS :**

➢ **Part (1) :determination of physicochemicalparameters in wastewater.**

1-Indicate the importance of determining the followingphysicochemicalparameters (indicate the information provided by eachparameteranalyzed):

TSS, COD, BOD_5, NT or NTK, PT.

3- Fill in the following table -1- with the resultsobtainedduring the measurementscarried out :

Type of water to	TSS	COD (TP01)	BOD_5 (TP02)

beexamined	**(mg/L)**	**(mgO_2/L)**	**(mgO_2/L)**
Wastewater 1			
Wastewater2			
River water			
Water …………..			

3- from the analyses obtained, calculate the following ratios and indicatetheirsignificance in the followingtable:

Type of water to beexamined➔	Wastwater 1	Wastwater 2	Water ………………..	**Importance or information provided by this report**
COD/BOD(biodegradability index)				

➢ <u>Partie 2 :</u>determination of permanganate index (IP)

1- Write down the redox half-equations for $MnO_4^-(aq)/Mn^{2+}(aq)$ and $CO_2(aq)/C_2O_4^{2-}(aq)$. Deduce the equation for the reactionbetween permanganate and oxalate ions in an acid medium.

2-

2.a. Draw up progress tables for the reactions in steps 2 and 3, noting :

- n_1 the quantity of permanganate ions introducedinto the Erlenmeyer flask;
- n_0 the quantity of permanganate ions reactedwith the organicmatter;
- n_2 the quantity of oxalate ions introducedinto the Erlenmeyer flask
- n_{rest} the quantity of oxalate ions remaining at the start of step 3
- n_E the quantity of permanganate ions added for V = V_E (step 3).

2.b. Show that : $$n_0 = n_1 - \frac{2}{5}.n_2 + n_E$$

2.c. Deducethat $n_0 = n_E$thencalculate n_0.

3.a. Deduce the quantity n_{e^-} of electronsused to oxidizeorganicmatter.

3.b. Calculate the quantity and then the mass of oxygen "O" thatwouldreactwiththeseelectronsaccording to the half-equation:

$$O + 2e^- = O^{2-}$$

3.c. Deduce the permanganate index of the sample.

NB : To determine the value of volume V_2, the concentration (or titre) of potassium permanganate used as the titrating solution must beverified

TP04 :
COAGULATION-FLOCCULATION TEST
(Jar-test)

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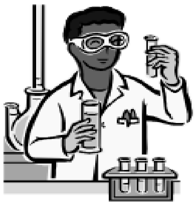
MASTER 2: ENVIRONMENTAL PROCESS ENGINEERING
TP: PHYSICO-CHEMICAL AND BIOLOGICAL TREATMENT OF WASTEWATER



TP N 04 :
COAGULATION-FLOCCULATION TEST
(Jar-test)

- INTRODUCTION :

The coagulation-flocculation process facilitates the removal of suspendedsolids and colloidalparticles

The coagulation-flocculation process facilitates the removal of suspendedsolids and colloidalparticles (sizes below 1µm), whichiswhy coagulation-flocculation can beused in the water treatment process to reduceturbidity. To treat water for potabilization, the coagulation-flocculation process requiresrigorouselimination of flocs, and must becoupledwithdecantation. Reagents must bepreciselydosed to avoidresidualmatter in the produced water.

Coagulation (the destabilization of colloidalparticles by the addition of a chemicalreagentknown as a coagulant) eliminates repulsions linked to the electronegativity of colloids. This isachieved by addingelectropositivemetalsalts, whichbind to the colloids and neutralizethem, thuscanceling the Zeta potential (Characteristic of the repulsive forces betweenparticles. Determined by measuring the displacementvelocity of a particlesubjected to an electricfield) of thesecolloids.

Secondly, flocculation causes colloidalparticles to agglomerate. Because of theirlowweight, individualparticles are unable to settle, and by creatingagglomerates (known as flocs), we can significantlyincrease the weight of the particles, makingthem large enough to settle.

Factorsthat can improve coagulation-flocculation are :

- time and velocity gradient are important for increasing the probability of particle clashes.
- and pH is a very important factor for colloidremoval.

- PURPOSE :

- Determine the optimum dose of coagulant and optimize the pH value to ensurethat the coagulation-flocculation process is effective in treatingpolluted water (effluent).

- MATERIALS, MEASURING EQUIPMENT AND PRODUCTS:

Materials, Measuringequipment	Products
- Graduated pipette + pro-pipette	- Sample water (polluted)
- 100ml, 250ml and 1L volumetricflasks.	- Distilled water + bentonite
- 06 beakers (900 ml).	- $Al_2(SO_4)_3.18H_2O$ at 10g/L
- Thermometer or electro-metric probe.	- $FeCl_3$ at 10g/L

- pHmeter. - Turbidimeter.	- Polyelectrolyte at 1g/L - HCl 1M - 1M NaOH

- HANDLING (Operating mode) :

✓ <u>Part1 :</u>Finding the optimal coagulant dose

6- Prepare 3L of a clay suspension (bentonite) at 200 mg/L or take 3L of polluted water for treatment.

7- Prepare 100ml of a solution of $Al_2(SO_4)_3.18H_2O$ at 10g/L (coagulant-1) or $FeCl_3$ at 10g/L (coagulant-2), $FeSO_4$ at 10g/L (coagulant-3), $CuSO_4$ at 10g/L (coagulant-4).Introduire dans chaque bécher de 900ml :

Sample (Beaker no.)	1 (witness)	2	3	4	5	6	7
Volume of polluted water (ml)	**500**	**500**	**500**	**500**	**500**	**500**	**500**
Coagulant volume-1 or 2, 3 or 4 « V_p » à 10g/L	**0ml**	**2,5ml**	**5ml**	**7,5ml**	**10ml**	**15ml**	**20ml**

3-Measure pH and turbidity (T_0) of sample 1 (control).

4- Place the 06 beakersunderrapid agitation (150 rpm) for 3 min.

5-Reduce agitation to 40 rpm for 15 min (or 30 rpm for 20 min) and observe, from time to time, for floc formation and quality.

6- Stop stirring and leave the mixture to stand for 30 min.

7- Pipette approximately 50 ml of supernatant to measureturbidity (Ti) and final pH.

8-Filter on pre-weighedfilterpaper (m_0), dry at 110°C and weigh the quantity of sludgeobtained**(m_1-m_0)**.

✓ <u>Part 2 :</u>Finding the right pH for coagulation-flocculationoperation

1- Prepare 3L of a clay suspension (bentonite) at 200 mg/L or take 3L of polluted water for treatment.

2- Prepare 100ml of a solution of $Al_2(SO_4)_3.18H2O$ at 10g/L (coagulant-1) or $FeCl_3$ at 10g/L (coagulant-2), $FeSO_4$ at 10g/L (coagulant-3), $CuSO_4$ at 10g/L (coagulant-4).

3- Introduceintoeach 900ml beaker, adjusting pH withHClacid solution (1M) and NaOH base solution (1M):

Sample (Beaker no.)	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Volume of polluted water	500	500	500	500	500	500	500

(ml)							
Coagulant volume-1 or 2, 3 or 4 « V_p » à 10g/L **(optimum dose)**	**2.5ml**	**2,5ml**	**2.5ml**	**2.5ml**	**2.5ml**	**2.5ml**	**2.5ml**
$pH_{initiale}$	**6**	**7**	**8**	**9**	**10**	**11**	**12**

Place the 06 beakersunderrapid agitation (**150 rpm**) for **3 min**.

5-Reduce agitation to **40 rpm** for **15 min** (or 30 rpm for 20 min) and observe, from time to time, for floc formation and quality.

6- Stop stirring and leave the mixture to stand for **30 min**.

7- Pipette approximately 50 ml of supernatant to measureturbidity**(Ti)** and **final pH**.

- **QUESTIONS :**

1- Fill in the followingtable:**(partie-1)**

Sample (Beaker no.)	**1 (témoin)**	**2**	**3**	**4**	**5**	**6**
Coagulant volume-1 or 2, 3 or 4 « V_p » à 10g/L	**0ml**	**2,5ml**	**5ml**	**7,5ml**	**10ml**	**15ml**
Coagulant dose -1 or 2, 3 or 4 "C_f"(mg/L)	…………..	…………..	…………..	…………..	…………..	…………..
pH_{finale}	…………..	…………..	…………..	…………..	…………..	…………..
Turbidity « Ti » (NTU)	…………..	…………..	…………..	…………..	…………..	…………..
(T_0-Ti)x 100/T_0 (efficiency)	…………..	…………..	…………..	…………..	…………..	…………..
TSS (mg/L)	…………..	…………..	…………..	…………..	…………..	…………..

2- Plot in the samegraph: (eitherwith**Regressi®** software or on millimetricpaper)
   - pHfinale= f(Cf)
   - Ti=f(Cf).

3- Deduce the value of the optimum dose (Coptim in mg/L) of the coagulant used to treat the polluted water.

4- Plot in the samegraph: (eitherwith Regressi® software or on millimetricpaper)
   Max Efficiency =f(Cf of each coagulant) or **Max Efficiency =f(coagulant type).**

5- Providedyou'vecarried out the experimentwith all 04 coagulants. Which of these 04 is the most effective for this type of water treated by the coagulation-flocculationtest?

6- Fill in the following table with the resultsobtainedduring the measurementscarried out :**(part-2)**

Sample (Beaker no.)	**1**	**2**	**3**	**4**	**5**	**6**
Coagulant volume-1 or 2, 3 or 4 « V_p » à 10g/L **(optimum dose)**	**2.5ml**	**2,5ml**	**2.5ml**	**2.5ml**	**2.5ml**	**2.5ml**
pH finale	………..	………..	………..	………..	………..	………..
Turbidity « Ti » (NTU)	………..	………..	………..	………..	………..	………..

(T_0-Ti)x 100/T_0 (efficiency)	………..	………..	………..	………..	………..	………..

7- Plot in the samegraph: (eitherwith**Regressi®** software or on millimetricpaper)
Ti= f(pHfinal)

8- Deduce the optimum pH value?

9- Conclude.

TP05 :
DECANTATION TEST-Part 1
(KYNCH's Law)

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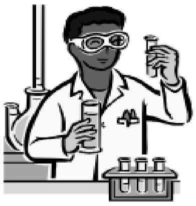


TP N 05 :
DECANTATION TEST-Part 1
(KYNCH's Law)

- **INTRODUCTION :**

There are two types of settling:
- **Settling of discreteparticles (grit):** of the same size and origin.
- **Decantation of flocculentparticles:** the falling speed of flocculentparticlesincreases as particleagglomerationincreases.

✓ *Settling of discreteparticles:*

Discreteparticlesettlingconsists in eliminatingparticles of the same size and origin.
As the particlefalls, itissubjected to three forces
- The force of gravity.
- Archimedeanthrust.
- Frictional forces.

There are various formulas for calculating the falling speed of a particle, depending on the flow regime (Reynolds number) in the settling tank. Different formulas for calculatingfallvelocity as a function of Reynolds number Re :

- For **10^{-4}<Re<1** (laminarregime for free-surface flows), the fallingvelocityisgiven by Stockes' formula:

$$Vp=\frac{d^2.(\rho_p-\rho_l).g}{18.\mu}$$

where: d: particlediameter, µ: dynamicviscosity of liquid, ρp: particledensity and ρl: liquiddensity.

- For **1<Re<500**, intermediate case equation:

$$Vp=\frac{0,153.g^{0,71}.d^{1,14}(\rho_p-\rho_l)^{0,71}}{\rho_l^{0,29}.\mu^{0,43}}$$

- For **500<Re<10000** ; **Newton's**equation (for turbulent flow):

$$Vp=1,74\sqrt{\frac{g.d.(\rho_p-\rho_l}{\rho_l}}$$

✓ **Decantation of flocculentparticles:**

The sedimentation rate of particlesincreasesduringsettling, due to particleagglomeration. Differentmathematicalmodelsdescribethis type of settling.

There are 02 types of flocculatedparticlesettling:

- ⇨ *<u>Diffuse settling</u> (duringsettling, flocculation continues and Vpvelocityincreaseswhen the concentration of flocculatedmatterisbetween 50-500 mg/L).*
- ⇨ <u>*Piston settling*</u> (when the concentration of flocculatedparticles> 500mg/L, interactions between the particles are not negligible, sotheysettle at piston➔flocculation and settling can beimproved first, thenslowed down beyond a certain critical concentration, referred to as "slowedsettling").

- **PURPOSE :**

  Study vertical-flow piston settling of flocculatedparticles and plot the "kynch" curve.
- **MATERIALS, MEASURING EQUIPMENT AND PRODUCTS:**

Materials, Measuringequipment	**Products**
- 02 Glass measuringcylinders 1L or 2 L - Graduated pipette + pro-pipette - 100ml, 250ml and 1L volumetricflasks. - 04 900 ml beakers. - 03 Jar-test flocculators - Stopwatch	- Distilled water. - Bentonite 5g/L and 10g/L or otherclay. - $Al_2(SO_4)_3.18H_2O$ at 10g/L (coagulant 1) - $FeCl_3$ at 10g/L (coagulant 2)

- HANDLING (Operating mode) :

1- Prepare 1L of a clay suspension (bentonite) at 5g/L and 10 g/L each, or take 1L of sludge-ladenpolluted water for treatment.

2-Prepare 100ml of 10g/L $Al_2(SO_4)3.18H_2O$ (coagulant-1) or 10g/L $FeCl_3$ (coagulant-2) solution.

3-Introduceintoeach 900ml beaker :

	Bentonite (5g/L)		**Bentonite (10g/L)**	
Sample (Beaker no.)	**1**	**2**	**3**	**4**
Volume of polluted water (ml)	500	500	500	500
Coagulant volume-1 or 2, « V_p » à 10g/L **(optimum dose)**	**2.5ml**	**2,5ml**	**2.5ml**	**2.5ml**

1- Place the 04 beakersunderrapid agitation **(150 rpm)** for **3 min**.

2-Reduce agitation to **50 rpm** for **15 min** (or 30 rpm for 20 min) and observe from time to time to detect floc formation and quality.

3- Stop stirring and transfereach 02 beakers (2x 500ml suspension) directlyinto a 1L glass measuringcylinder.

4- Start the stopwatchwhen the last drop of suspension ispoured in.

5-During the decantingoperation, record the time **"t"**continuously in each test tube and read the volume (or height "H") at the moment of appearance of each interface formedbetween the particles and the clearliquid (water).

NB :don'tforget to take the dimensions (height "H" of the 1L test tubes and theirdiameters "d") whichwillbeuseful for the vertical flow decantationoperation.

- **QUESTIONS :**

1- Fill in the table with the resultsobtainedduring the measurements:

Test tube N°❶ : ➔	Bentonite (5g/L) + 2.5ml de coagulant 1 ou 2		Test tube N°❷ : ➔	Bentonite (5g/L) + 2.5ml de coagulant 1 ou 2	
Time(sec)	**Volume read(ml)**	**Height « H » (m)**	**Time (sec)**	**Volume read(ml)**	**Height « H » (m)**
t_0=0.00	1000	H_0= ………..	t_0=0.00	1000	H_0= ………..
t_1=……….			t_1=……….		
t_2=……….			t_2=……….		
t_3=……….			t_3=……….		
t_4, t_5, t_6…..			t_4, t_5, t_6…..		

NB :itispreferable to use the **Regavi®** software afterfilming all the settlingoperationscarried out in the Laboratory (to ensureproper monitoring of the settlingoperation and, above all, good observation of the fall of particles, as well as accuratereading of volume and height).

2- Draw the 02 graphs: (eitherwith***Regressi®*** software or on millimetricpaper)

- **H= f(t) (kynchcurve)** and **V=(t)**. forspecimens❶ **and** ❷**.**

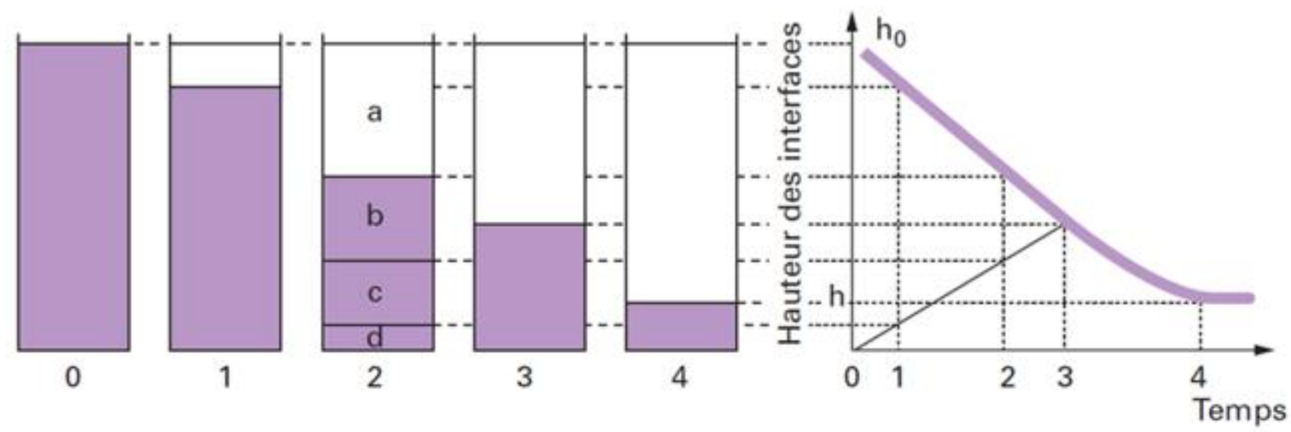
3- Interpret the 02 graphs (indicatewhetherthereis a flake coalescence phase) see APPENDIX .

4- Graphicallydeduce the velocity "V" at which the particlesfallinto the 02 test tubes (seeAPPENDIX).

5- Are thereothermethods of studying the settling of flocculatedparticles? If so, please list them.

APPENDIX

When piston decantationisperformed in a tube of sufficientheight and diameter (at least a one-liter test tube), four zones are generallyobserved (Figure 1).



a : Zone de clarification où le liquide est clair.
b : Zone de suspension homogène de même aspect que la solution de départ avec une interface a-b nette.
c : Zone de transition (pas toujours observable).
d : Zone d'épaississement des boues dont le niveau augmente rapidement avant de diminuer lentement.

Figure 1:**Piston decantation: Kynchcurve**

At a certain point, zones b and c disappear - thisis the critical point. The evolution of the height of the a-b interface as a function of time forms the Kynchcurve.

⇨ ***Kynchcurve:***(figure 2)

Kynch'sfundamentalhypothesisisthat the speed at which a particlefallsdependsonly on the local concentration C of particles.

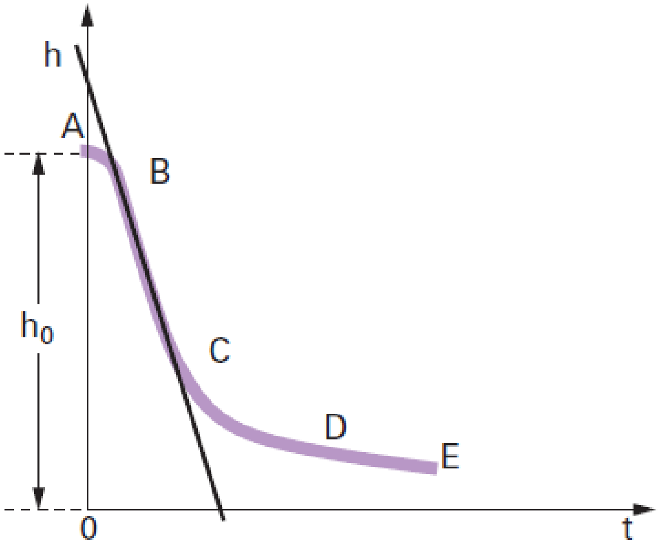


Figure 2. **Kynchcurve**

From A to B, the separation surface is more or lessclear:thisis the flake coalescence phase. This phase issometimes non-existent.

From B to C, a rectilinear section translates into a constant falling speed V(slope of the straight line). For a tube of given dimensions, V is a function of the initial TSS concentration and the flocculationcharacteristics of the suspension. As the initial concentration C increases, the settlingvelocity V of the mass decreases: for example, for an urbanactivatedsludgewhose TSS concentration increasesfrom 1 to 4 g - L-1, V decreasesfrom 6 to 1.8 m - h-1.

The upwardly concave CD section corresponds to a gradualslowdown in the rate of fall of the top layer of the deposit.

From D onwards, the flakes toucheachother, exerting compression on the lowerlayers.

Kynch'stheoryapplies to the BC and CD sections, which cover the essential area of flocculatedsludgesettling.

⇨ ***Interpretation:***

If weconsider a suspension whosesettlingdoes not include a coalescence phase (Figure 3), the calculation shows that :

- in the BOC triangle, concentration and fallvelocity are constant and equal to the initial values prevailing in B ;

- in the COD triangle, the equi-concentration curves are straight lines passing through the origin, whichmeansthatfrom the very first moments of settling, the layersclosest to the bottompassthrough all the concentrations between the initial concentration and thatcorresponding to point D,
the start of compression.

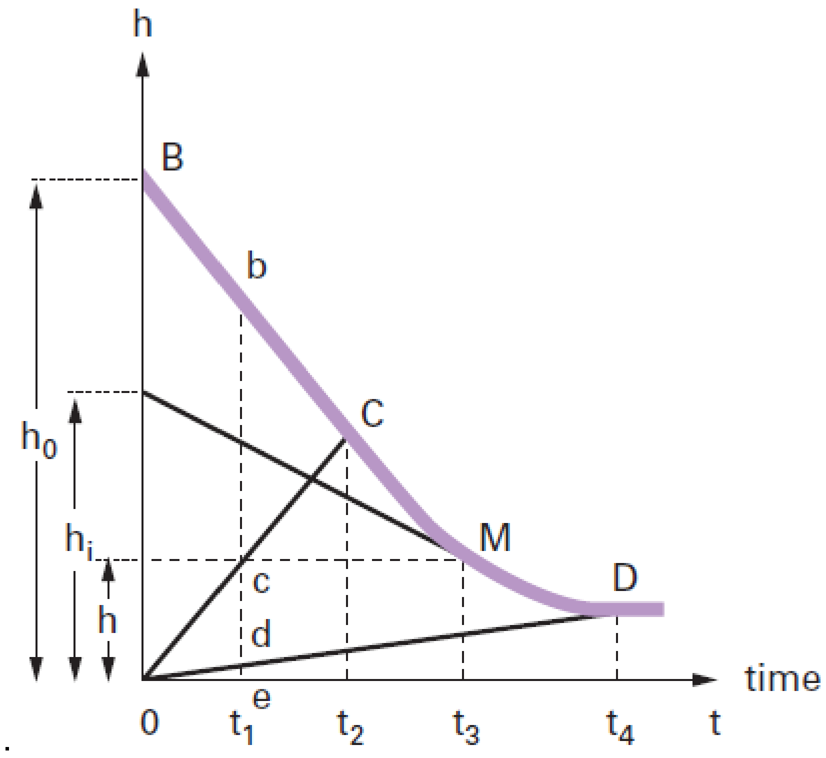


Figure 3. **Interpretation**

The muddy medium of heighteb at time t1 therefore has three distinct zones:

- an upper zone bcwhere concentration and fallvelocity are uniform and have retainedtheir initial values C and V0 ;
- an intermediate zone cd in which concentration increasesprogressivelyfrom c to d, and fallvelocitydecreasesaccordingly;
- a lower zone de where the sludge flakes are subjected to compression.

In the medium considered, the upper zone disappears at time t2, and only the lower zone remains at time t4.

For point M in part CD, two concentrations can bedefined:
CMi interface concentration,
CM average concentration.

According to Kynch'shypothesis :

$$C_M^i = C_0 . \frac{h_0}{h_i}$$

In addition :

$$C_M = C_0 . \frac{h_0}{h}$$

The three parts BC, CD and DE of the Kynchcurve (Fig. 2) are applied to the calculation of slowedsedimentation structures. Phase BC corresponds to sludge-contact decanters.

The CD phase relates to structures wheresludge concentration isrequired (thickenedsludge recirculation devices). The DE phase isused for sludgethickening.

TP06 :
DECANTATION TEST-Part 2
(MOHLMAN Index and DSVI)

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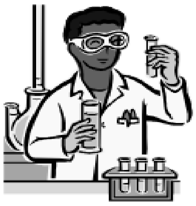

TP N 06 :
DECANTATION TEST-Part 2
(MOHLMAN Index and DSVI)

- **INTRODUCTION :**

The treatmentsludgeformedisobtainedafter the coagulation-flocculationreaction or biologicaltreatmentwithactivatedsludge. Itsquantity and settleability (solid-liquidseparation) can beestimatedusing the Mohlman index. In general, an easilysettleablesludge has a Mohlman Index (MI) of between 50 and 150 mL/g, with a TSS concentration in the sludge of between 1,500 and 2,500 mg/L.
The MOHLMAN "I_M" (**S**ludge**V**olume **I**ndex) isdefined as the volume occupiedafter 30 minutes settling of a sludgesamplecorresponding to 1 gram of dry matter.
This index isrepresented by the ratio: volume of sludgesettledin 30 minutes (mL/L) / mass of dry matter (g/L).
- The MOHLMAN index isused to characterizesludgedilatability,
*A normal sludge has an index of 100. In the presence of bulking, the index increases, reaching a value of 500.
- If there are problemswith clarifier settling, the sludgeshouldbeexaminedmicroscopically.isdefined as the volume occupiedafter 30 minutes settling of a sludgesamplecorresponding to 1 gram of dry matter.
This index isrepresented by the ratio: volume of sludgesettledin 30 minutes (mL/L) / mass of dry matter (g/L).
- The MOHLMAN index isused to characterizesludgedilatability,
*A normal sludge has an index of 100. In the presence of bulking, the index increases, reaching a value of 500.
- If there are problemswith clarifier settling, the sludgeshouldbeexaminedmicroscopically.
- The MOHLMAN index isonlytrulyrepresentative of a sludge'sdilatability if :
*the final volume obtained, from an initial volume of 1L, isbetween 100-250mL. In this range, the index isproportional to the sludge concentration.
L'indice de boues « I_B »(ou **D**iluted**S**ludge**V**olume **I**ndex) est défini à partir de tests de décantation permettant d'obtenir des volumes de boues compris entre 100-250mL

- **PURPOSE :**
  - Determine the **MOHLMAN index (I_M or SVI)** of water from the aeration tank.
  - Determine the **Sludge Index (I_B or DSVI)** of water from the aeration tank.

- MATERIALS, MEASURING EQUIPMENT AND PRODUCTS:

Materials, Measuringequipment	Products
- 04 IMHOFF cone or 04 1L glass measuringcylinders - Graduated pipette + pro-pipette - 100ml, 250ml and 1L volumetricflasks. - 04 900ml beakers. - Filterpaper - Funnels (GM) - Stopwatch. - Data processing software (Regavi®, Avimeca®.....etc)	- Distilled water. - Muddy water (sludge) fromaeration tank after 15 or 20 min of operation. - Bentonite 5g/L and 10g/L or otherclay.

- HANDLING (Operating mode) :

Important note:

Beforehand, measure the "TSS" of the muddy water (sludge) comingfrom the aerator (take an aliquot) see TP01 on physicochemical and biologicaltreatment of wastewater.

8- Perform the followingoperations:

- **Part A :determination of the MOHLMAN index (I_M or SVI).**

a- a- Transfer the slurry to a 1000 mL test tube or IMHOFF cone.

b- b- Allow to settle and monitor sludge height every 5 minutes.

c- c- Determine the volume of sludge at **t = 30 minutes.**

Figure 1: IMHOFF cone

Expression of results:

$$I_M = \frac{V_{30}}{MES}$$

V_{30} ou V :volume of sludgeafter**30 min**settling (cm^3 or ml),
MES or (TSS) : present in this volume (g).

- **Part B :determination of the sludge index (IB or DSVI).**

a- Introduceintoeach 1000ml test tube:

	Sample (Test piece no.)	❶	❷	❸
STEP-Sidi Bel Abbes	Volume of muddy water **(ml)** in aeration tank	500	250	125

b- Fill test tubes to **1 L**with water takenfrom the clarifier outlet (secondary clarifier).
c-Homogenize the contents of the test tubes by invertingthemseveral times aftersealing.
d- Let settleafter**30 min**.
e- Start the stopwatchwhen the last drop of suspension ispoured.
f-During the decantingoperation, record the time **"t"**continuously in each test tube and read the volume (or height "H") at the moment of appearance of each interface formedbetween the particles and the clearliquid (water).

NB :don'tforget to take the dimensions (height "H" of the 1L test tubes and theirdiameters "d") whichwillbeuseful for the vertical flow decantationoperation.

Expression of results:

$$I_B = \frac{V_{30}}{(MES)_a \cdot f}$$

V_{30} ou V :sludge volume after**30 min**settling (cm^3/L or ml/L),
(MES)aor (TSS) : present in this volume (g/L dry matter).
f **:** dilution factor **(volume of sludgeinitiallyintroducedinto the test tube in mL/1000)**

- **QUESTIONS :**

1- Fill in the following table with the resultsobtainedduring the measurementscarriedout:

Nature of wastewater to beexamined	m_0 (in mg)	m_1 (in mg)	TSS (mg/L)
Aeration tank water			
…………….. etc			

2-Calculate the MOHLMAN index "I_M" (ml/g).
3-Based on the "IM" value obtained, isitnecessary to move on to measuring "IB"?
4-Define the **bulking**problem.
5- This parameterisused to size one of the wastewatertreatment stages. Whichone?
6- This index isuseful for determininganotherparametercharacterizing the sludge. Whichisit?
7- Fill in the table with the resultsobtainedduring the "IB" measurements:

Test tube N°❶ : ➔	500ml muddy water + q.s.p 1L water.		Test tube N°❷ : ➔	250ml muddy water + q.s.p 1L water.		Test tube N°❸ : ➔	125ml muddy water + q.s.p 1L water.	
Time (sec)	**Volume read(ml)**	**Height « H » (m)**	**Time (sec)**	**Volume read(ml)**	**Height « H » (m)**	**Time (sec)**	**Volume read(ml)**	**Height « H » (m)**
t_0=0.00	1000	H_0=….	t_0=0.00	1000	H_0=….	t_0=0.00	1000	H_0=….
t_1=………..			t_1=………..			t_1=………..		
t_2=………..			t_2=………..			t_2=………..		
t_3=………..			t_3=………..			t_3=………..		
t_4, t_5, t_6…..			t_4, t_5, t_6…..			t_4, t_5, t_6…..		

NB :itispreferable to use the ***Regavi***® software afterfilming all the settlingoperationscarried out in the Laboratory (to ensureproper monitoring of the settlingoperation and, above all, good observation of the fall of particles, as well as accuratereading of volume and height).

2- Plot the graph: (eitherwith Regressi® software or on millimetricpaper)
H= f(t) (kynchcurve) or V=(t). for test specimens❶ **and** ❷ **and** ❸.

3- Determine the "IB" (DSVI) of each test piece by filling in the followingresultstable:

Aeration tank water	**Sample (Test piece no.)**	❶	❷	❸
	f (dilution factor)			
	V30			
	$(TSS)_{B.aeration}$			
	I_B (DSVI) inml/g			

4- Conclude (whatis the settlingquality of thismuddywater? good, average, poor) -see **APPENDIX.**

APPENDIX

MohlmanIndex(sludge volume index : SVI)

A particular point isconsidered on the Kynchcurve, that of the 30-minute abscissa: the **Mohl¬man index** "I_M" iswidelyused to characterize the settleability of biologicalsludge and therefore for clarifier sizing, or even the triggering of corrective methods if overflowdevelops.

$$I_M = \frac{V_{30}}{MES}$$

V_{30}or V :volume of sludgeafter 30 min settling (cm^3 or ml),
MES or (TSS) : present in this volume (g).

The disadvantage of Mohlman's index isthatitishighlydependent on the initial sludge concentration. Methods have therefore been proposed to define an index thatisindependent of this concentration, and thereforecharacteristiconly of the state of the sludge in the plant.

These are :

(IB) or dilutedMohlman index (DSVI).

The Kynchcurveisdeterminedafter dilutions to recover a sludge volume, after 30 min settling, in the vicinity of 200-250 mL per L.
The "DSVI" sludge index used in France isvalid if this volume isbetween 100 and 300 mL, the DSVI used by the Anglo-Saxons if itisbetween 150 and 250 mL. In both cases, activatedsludge can besaid to have very**good settleability**whenitssludge index or DSVI isbetween 50 and 100 cm^3g^{-1}, **normal settleability**between 100 and 200, and **poor settleability**above 250.

TP07 :
DISINFECTION TEST
(chlorinedemand - "break point" method)

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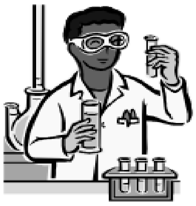
TP: PHYSICO-CHEMICAL AND BIOLOGICAL TREATMENT OF WASTEWATER



TP N 07 :
DISINFECTION TEST
(chlorinedemand - "break point" method)

- **INTRODUCTION :**

This is the final stage in the treatmentchain, eliminating all pathogenicmicro-organismsfrom the water, as well as someorganic and mineral pollution. A few commongermsmayremain in the water, as disinfectionis not sterilization.

Chlorineisused for disinfection, so a certain level of residualchlorine must beinjected to killanygermsthat can berevived.

It isgenerallyacceptedthatdisinfectionis the final stage in a treatmentchain, wherechlorinepenetratesmicro-organismssuch as bacteria or viruses and destroys them by inhibiting certain vital synthesisreactions. Manyenvironmentalfactors influence the effectivenesswithwhichchlorinedisinfects water, including water temperature, pH, contact time, degree of mixing, turbidity, undesirable substances and availablechlorine concentration.

The contact time or action time of sodium hypochlorite is at least half an hour, but if the temperatureisonlybetween 10 and 18°C, the contact time must be at least one hour, and longer if the temperatureisbelow 10°C.

Belowis the curverepresenting the "breakpoint" test to determine the optimum chlorine dose needed to eliminate all the nitrogenousmatter (organic and mineral) thatgivesourtreated water an unpleasant taste.

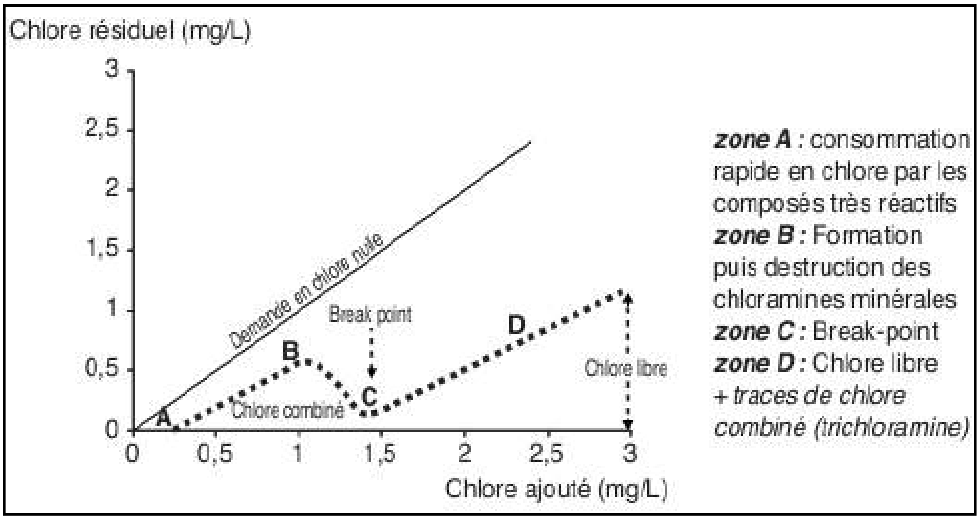


Figure 2 : curverepresenting the break point of disinfectednatural water.

This curve (Figure 1) issubdividedinto 03 zones:

1st zone:represents the increase in residualchlorine due to the formation of chlor-amines and organochlorines.
2nd zone: shows the decrease in residualchlorine due to the destruction of chlor-amines.
3rd zone:reveals the quasi-lineargrowth of residualchlorine due to the formation of free chlorine effective for disinfection.

- **PRINCIPLE :**

  Residualchlorine in water isoftenanalyzed by the volumetric or iodometricmethod, the latter involving a highlyacidic medium (3 <pH<4) by introducing iodide ions (I-, transparent color), thendosing the iodine (I_2, yellowcolor) released by sodium thiosulfate ($Na_2S_2O_3$). This enables chlorine in Cl_2form to bedetermined. The results correspond to oxidizingequivalents (HClO, ClO^-) expressed in mgCl_2/L.

- **PURPOSE :**

  Determine the precise**dose of chlorine**required for a volume V of water using the **break-point method** (total degradation of ammoniacal nitrogen - lowestresidualchlorine value).

- **MATERIALS, MEASURING EQUIPMENT AND PRODUCTS:**

Materials, Measuringequipment	Products
- 02 Graduated burettes - 02 Graduated micro-burettes - Graduated pipettes + pro-pipette - 100ml, 250ml and 1L volumetricflasks. - 20 Erlenmeyer flasks or 150ml flasks. - Magnetic stirrers - Magnetic stirrers	- Distilled water. - Surface or dam water or treated water. - Sodium thiosulfate (0.01M). - Sodium thiosulfate (0.1M). - Potassium iodide 0.1M (KI). - Starchstarch (10g/L). - Glacial CH_3COOH (5M). - H_2SO_4 (1M) - Bleach (Ch°12)

- **HANDLING (Operating mode):**

- **Important note:**

  Carry out a chlorometric control (Chl°) of the bleachyou are going to use to determine the breakpoint.

  Perform the followingoperations :

  - **Part A :control of chlorometricdegree (Chl°) of bleach**

1-From the commercial bleach solution (S_0) of concentration C_0, prepare 100ml of a solution (S) of concentration $C = C_0/10$. (10 times diluted).
2-Into an Erlenmeyer flask, introduce :
- 10ml solution (S).
- 10 ml glacial aceticacid (5M) or sulfuricacid (H_2SO_4), concentration 1M.
- 20 ml potassium iodide solution (KI), concentration C_1= 0.1M.

3-Introduce a bar magnet and a few drops of starch paste. Homogenize the mixture using a magneticstirrer.
4- Fill burette with sodium thiosulfate solution ($Na_2S_2O_3$) with $C_2 = C_{S2O3^-} = 0.1$ M=0.1N.
5-Graduallyadd sodium thiosulfate until the mixture isdiscolored to the drop. Note the volume poured**Ve(A)** or **$Ve_{(S2O3-2)}$**.

Expression of results:

$$[Cl_2]_{Actif}\,(g/L) = \frac{C_{S_2O_3^{-2}}\,V_{e(S_2O_3^{-2})}}{V_{echantillon-eau-javel-dilué}}\,(M_{Cl_2}/2)$$

Or

$$[Cl_2]_{Actif}\,(mg/L) = 35,5*10^3\,\frac{C_{S_2O_3^{-2}}\,V_{e(S_2O_3^{-2})}}{V_{echantillon-eau-javel-dilué}}$$

$V_{e(A)}$ or $V_{e(S2O3^{-2})}$.:volume of sodium thiosulfate ($Na_2S_2O_3$) added at equivalence point (ml),
V_{sample}: volume of dilutedbleach test sample (ml)
$M(Cl_2)$= (35.5 * 2)=71 g.mol^{-1}
Thus: (withbleach dilution factor = 10 times)

$$C_0\,(mg/L) = 10.\left[35,5*10^3\,\frac{C_{S_2O_3^{-2}}\,V_{e(S_2O_3^{-2})}}{V_{echantillon-eau-javel-dilué}}\right]$$

Hence :

$$Chl° = \frac{C_0\,(mg/L_{eau-javel})}{3,17.10^3\,(mg/L_{eau-javel})}$$

➢ Part B :chlorineresidualmeasurement (break-point test)

a- This time, fill the burette with sodium thiosulfate solution ($Na_2S_2O_3^-$ 0.01N).
b-According to the following table, introduceintoeachbeaker or Erlenmeyer flask (150ml): (the 15chl° bleachusedis 100 times diluted (solution "S'" i.e. 0.48 g/L).

NB :for bleachwithchlorometricdegreesotherthan 15 chl°, the volumes to bewithdrawn are listed in APPENDIX.

Samples➔ (bekersN°)	❶	❷	❸	❹	❺	❻	❼	❽	❾	❿
Volume**(V'p)**of Cl_2added at**100 ml treated water**	**0.105**	**0.157**	**0.210**	**0.315**	**0.368**	**0.420**	**0.630**	**0.841**	**1.051**	**1.261**
Samples➔ (bekersN°)	⓫	⓬	⓭	⓮	⓯	⓰	⓱	⓲	⓳	⓴
Volume**(V'p)**of Cl_2added at**100 ml treated water**	**1.472**	**1.682**	**1.892**	**2.103**	**2.313**	**2.523**	**2.734**	**2.944**	**3.154**	**4.206**

a- Shake and cap Erlenmeyer flasks or beakers.
b- Place the Erlenmeyer flasks or beakers in a dark place.
c-Leavetheseflasks (erlenmeyer flasks or beakers) for a defined contact time (here 30 min or 1h).
d-Takefromeachbeaker or Erlenmeyer :
- 10 ml chlorine-treated water sample

- 20 ml sulfuricacid (H_2SO_4, 1M) or 20 ml glacial aceticacid (CH_3COOH, 5M).
- 20 ml potassium iodide solution (KI), concentration C_1= 0.1M.

e-Performvolumetric titration of all prepared solutions with sodium thiosulfate titrant solution ($Na_2S_2O_3$, 0.01M) until the yellowcolordisappears (or the bluecolordisappears if youused 10g/L starchstarch).

f- Note the volume poured at equivalence**$V_{e(B)}$**

NB :To find out how muchbleach to add to achieve the desired concentration, youneed to know the chlorometric value, whichshouldbeindicated on the bottle (althoughbeware of the reliability of this information and of counterfeiting in some countries).

One chlorometricdegree corresponds to ➔ 3.17 grams of active chlorine per liter of bleachunder C.N.T.P. conditions (1atm and 273°K).

Therefore, if the bleachavailableis at Chl°, and if youwish to obtain a concentration "C" or (**$[Cl]_{Active}$** or Added in mg/L) of active chlorine in the water to betreated (between 5 and 20mg/L, depending on the case), the volume of bleach to beadded can beeasilycalculatedusing the followingformula:

$$V_{bleach}\ (ou\ V_p) = C * V_{watertreated} / (3{,}17\ 10^3 * chl°)$$

The resultobtainedis in ml if the concentration wasexpressed in mg/L.

✓ If the bleachisdiluted "n times", the new volume to beaddediscalculatedusing the followingformula: $V'_{eau\ de\ javel}(ou\ V'_p) = n * V_{eau\ de\ javel}$

- **QUESTIONS :**

➢ **Part A :control of chlorometricdegree (Chl°) of bleach**

- Fill in the following table of results: (the 15chl°bleachusedis 10 times diluted ("S" solution, i.e. **4.8 g/L**).

$V_{e(A)}$ in ml	$[Cl_2]_{actif\ diluted}$ in mg/L	C_0 in mg/L	Chl°

➢ **Part B :chlorineresidualmeasurement (break-point test)**

5- Fill in the following table with the resultsobtainedduring the measurementscarriedout: (the 15chl° bleachusedis 100 times diluted (solution **"S'"** i.e. **0.48 g/L**).

Samples➔ (bekersN°)	❶	❷	❸	❹	❺	❻	❼	❽	❾	❿
Concentration "C" of active or addedchlorine (mg/l)	0.5	0.75	1	1.5	1.75	2	3	4	5	6
Volume**(V'p)** de Cl_2 ajouté à **100 ml d'eau à traité**	0.105	0.157	0.210	0.315	0.368	0.420	0.630	0.841	1.051	1.261
$Ve_{(B)}$(chlorineresidual measurement) **in ml**										
$[Cl_2]_{résiduel}$in mg/L (Total residualchlorine concentration)										
Samples➔ (bekersN°)	⓫	⓬	⓭	⓮	⓯	⓰	⓱	⓲	⓳	⓴

Concentration "C" of active or addedchlorine (mg/l)	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**20**
Volume**(V'p)** de Cl_2 ajouté à **100 ml d'eau à traité**	**1.472**	**1.682**	**1.892**	**2.103**	**2.313**	**2.523**	**2.734**	**2.944**	**3.154**	**4.206**
$Ve_{(B)}$(chlorineresidual measurement) **in ml**										
$[Cl_2]_{résiduel}$in mg/L (Total residualchlorine concentration)										

2-Draw the graph: (eitherwith***Regressi®*** software or on millimetricpaper)
$[Cl_2]_{Totalresidual}$ (mg/L)= f($[Cl_2]_{\text{Active or Added in mg/L}}$)
3-From the graph, determine the coordinates of the breakpoint.
4-Calculate the amount of chlorineconsumed (mg/L) at the breakpoint.

Expression of results:

$$[Cl_2]_{consommé}(mg / L) = [Cl_2]_{ajouter}(mg / L) - [Cl_2]_{residuel}(mg / L)$$

5-Whatis the differencebetween**"sterilization"** and **"disinfection"**?
6-Conclude (compare the value of chlorineactuallyconsumedwiththatindicated in the theory**7.6 mg/L**)

APPENDIX

The volumes to betaken for a 12Chl° bleach (100 times diluted, solution "S'" i.e. 0.38 g/L).

Samples➔ (bekersN°)	❶	❷	❸	❹	❺	❻	❼	❽	❾	❿
Volume**(V'p)**of Cl_2added at**100 ml treated water**	**0.131**	**0.197**	**0.263**	**0.394**	**0.460**	**0.526**	**0.789**	**1.052**	**1.315**	**1.579**
Samples➔ (bekersN°)	⓫	⓬	⓭	⓮	⓯	⓰	⓱	⓲	⓳	⓴
Volume**(V'p)**of Cl_2added at**100 ml treated water**	**1.842**	**2.105**	**2.368**	**2.631**	**2.894**	**3.158**	**3.421**	**3.684**	**3.947**	**5.263**

The volumes to betaken for 16Chl° bleach (100 times diluted, solution "S'" i.e. 0.51 g/L).

Samples➔ (bekersN°)	❶	❷	❸	❹	❺	❻	❼	❽	❾	❿
Volume**(V'p)**of Cl_2added at**100 ml treated water**	**0.100**	**0.150**	**0.200**	**0.295**	**0.345**	**0.400**	**0.600**	**0.788**	**0.986**	**1.183**
Samples➔ (bekersN°)	⓫	⓬	⓭	⓮	⓯	⓰	⓱	⓲	⓳	⓴
Volume**(V'p)**of Cl_2added at**100 ml treated water**	**1.380**	**1.577**	**1.775**	**1.971**	**2.170**	**2.366**	**2.563**	**2.760**	**3.000**	**3.943**

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