BURSA ULUDAĞ UNIVERSITY
FACULTY OF ENGINEERING
ENVIRONMENTAL ENGINEERING
DEPARTMENT

# CEV 3023 E UNIT OPERATIONS OF ENVIRONMENTAL ENGINEERING

## Experimental Procedures

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## EXPEROMENTAL PROCEDURES

## Content

## SLUDGE THICKENING

Thickening is a procedure used to increase the solids content of sludge by removing a portion of the liquid fraction. For example, if waste activated sludge, which is typically pumped from secondary tanks with a content of 0.8% solids, can be thickened to a content of 4% solids, then a fivefold decrease in sludge volume is achieved.

Thickening is generally accomplished by physical means including co-settling, gravity settling, flotation, centrifugation, gravity belt, and rotary drum. The volume reduction obtained by sludge concentration is beneficial to subsequent treatment processes, such as digestion, dewatering, drying and combustion from the following standpoints:

1. Capacity of tanks and equipment required
2. Quantity of chemicals required for sludge conditioning
3. Amount of heat required by digesters and amount of auxiliary fuel required for heat drying or incineration, or both.

Volume reduction is very desirable when liquid sludge is transported by tank trucks for direct application to land as a soil conditioner [1]. Thickened sludge still behaves as a liquid and can be pumped. However, the dewatered sludge generally behaves as a solid and can be trucked in most cases.

A thickener operates pretty much like a settling tank. The feed enters from the middle, are distributed radially, the settled sludge is collected from the underflow, the effluent exits over the weirs.

In a continuously operated thickener, there are different zones of concentration. The topmost zone is free of solids and comprises the liquid that eventually escapes over the weirs. The next zone is called the feed zone although this zone does not necessarily have the same concentration of feed solids. This zone is characterized by a uniform solids concentration. Below the feed zone is a zone of increasing solids concentration (from feed zone concentration to underflow concentration). This zone is compaction zone. Sludge blanket is defined as the top of the feed zone. The height of this blanket is the main operational control that the treatment plant operator has over the thickener. By increasing the underflow rate, the operator can lower the blanket, and hence the solids residence time is lowered, throughput of solids is increased and the solids concentration in the underflow is decreased. The operator then would have a higher reserve volume in case there is an unexpected heavy sludge load coming. A high sludge blanket will make the underflow solids concentration high due to high solids residence time.

### Design of Thickeners

The thickening process takes place in a settling tank with sufficient solids retention time. For example in secondary clarifiers of activated sludge systems both clarification and thickening operations are carried out. Actually, the thickening of the sludge is a concern to the operator where she/he desires a high underflow solids concentration. So it is the general practice to design these processes for both thickening and clarification performance.

## Thickener Design based on Laboratory Data

Typical test is done by using a 1000 mL-graduated cylinder. Sludge is mixed homogenously and let to settle in the cylinder. In seconds an interface separating the solids and the clear water on top is formed with a certain settling velocity. This velocity of the interface is measured with respect to time. Interface height is plotted against time and the zone settling velocity (ZSV) is calculated from the initial slope of the graph. The graph is given in Figure 1.

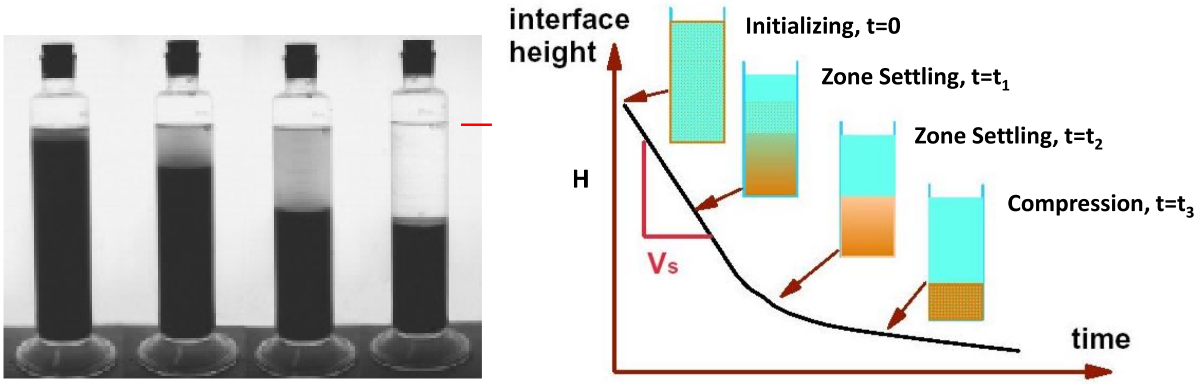
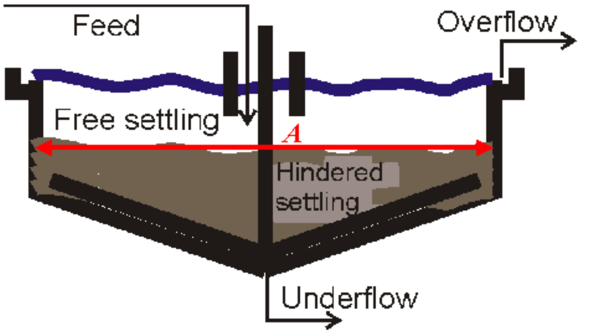


Figure 1. Zone settling in a thickener

The velocity with which solids settle out will depend on the concentration of solids. Right after time zero, there are two interfaces moving towards each other. One from the bottom up due to the building up layers of sludge from the bottom, the other interface is moving down from top to bottom, this is the blanket of settling sludge. Settling velocity, v is calculated at this time. At time t2, these will meet and settling will slow down. Then the settling will cease over time and compaction begins (Figure 2).



**Procedure gives the plan area of the thickener illustrated above, thickener depths are usually 2 to 4 metres.**

Figure 2. Hindered settling in a thickener

Talmage and Fitch procedure is applied to find the required area for a thickener. The procedure is as follows:

**Procedure:**

1. Determine the slope of the zone settling region (ZSV) (this is the settling velocity $\mathbf{V_s}$ for clarification). Use Table 1 to observe the settling.
2. Draw a figure and show zone settling region (Figure 3).
3. Extend the tangents from the ZSV region and compression region and bisect the angle formed to locate point 1.
4. Draw a tangent to the curve at point 1.
5. Knowns: Co, Ho, and select Cu, then make a mass balance

Cu.Hu = Co.Ho, calculate Hu from:

$$H_u = \frac{C_0 H_0}{C_u}$$

**5.** Draw a horizontal line from Hu until it intersects with the tangent line and determine tu. This is the time required to reach an underflow concentration.
**6.** Determine the area required for thickening (At)

$$A_t = 1.5(Q + R)\frac{t_u}{H_0}$$

where
Q = flowrate to the aeration tank excluding the recycle flow
R = recycled sludge flow
Q+R = total flow to the clarifier
1.5 = scale-up factor
7. Determine the area required for clarification (Ac)

$$A_c = 2.0\frac{Q}{ZSV}$$

Q = the effluent flow over the weir (same as above)
2.0 = scale-up factor

***"Whichever area is larger will govern the design and will be the design area."***

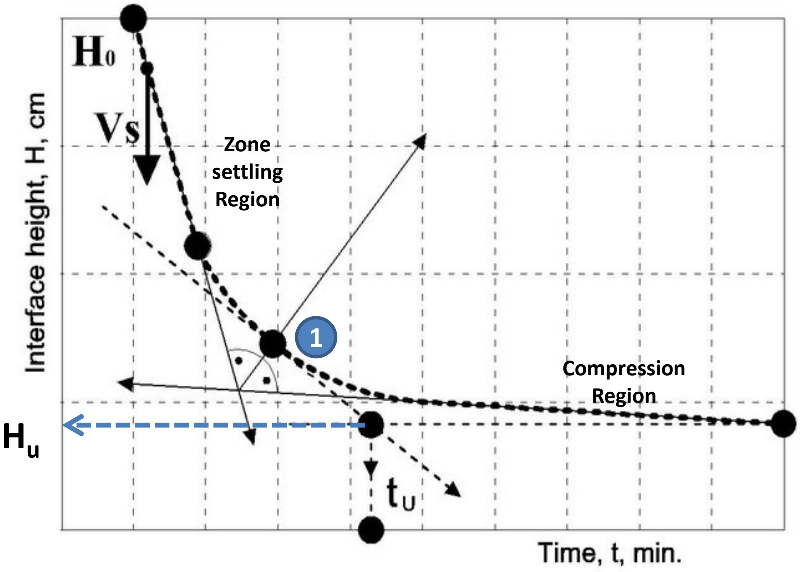


Figure 3. Talmage and Fitch procedure to find the required area

Table 1. Settling Velocity Table

| **Time<br>(minutes)** | **H<br>(cm)** | **Vs<br>(cm/min)** |
|---|---|---|
| | | |
| | | |
| | | |
| | | |
| | | |

## pH DETERMINATION

**Purpose of Experiment:** Learning the basics of potentiometric titration.

### 1. THEORY:

According to the acid-base theory, the proton donating substance is an acid. The substance that receives a proton is the base. According to this definition for acids and bases;

$NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$

Base Acid

In its reaction, $H_2O$ is an acid and $H^+$ gives the ion. This $H^+$ ion takes the base $NH_3$. As a result, $NH_4^+$ and $OH^-$ ions are formed. This reaction can be written in reverse. In the new reaction, $NH_4^+$ is an acid and $OH^-$ is a base.

$NH_4^+ + OH^- \longrightarrow NH_3 + H_2O$

Acid Base

A reversible reaction is indicated by a double arrow. In this written reaction, acids and bases can be expressed as follows.

$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$

Base(1) Acid(2) Acid(1) Base(2)

Wherein the $NH_3$ / $NH_4^+$ pair (1), $H_2O$ / $OH^-$ pair (2) are shown. These pairs are called conjugate pairs. Since $NH_3$ takes a proton, it becomes a base. The protonated form $NH_4^+$ is the conjugate acid of $NH_3$. Similarly, $H_2O$ is an acid and $OH^-$ is its conjugate base.

Ionization of acetic acid can be shown as follows;

$HC_2H_3O_2 + H_2O \rightleftarrows H_3O^+ + C_2H_3O_2^-$

Acid(1) Base(2) Acid(2) Base(1)

**pH and pOH Concept:** $[H_3O^+]$ and $[OH^-]$ whose products are equal to 1.0 x $10^{-14}$ are usually very small values. pH means the hydrogen ion potential and is the minus logarithm of $[H_3O^+]$.

$pH = -\log [H_3O^+]$

pOH is the minus logarithm of the hydroxyl ion concentration of $[OH^-]$.

$pOH = -\log [OH^-]$

pH + pOH =14

The pH is 7 since $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}$ M in pure water. Pure water and all aqueous solutions with a pH of 7 are neutral. If the pH value is less than 7.00, the aqueous solution is acidic, if the pH value is greater than 7.00, the aqueous solution is basic.

As the pH value approaches 0, the acidity feature increases, the further away from 0, the acidity feature decreases.

**Acid-Base Indicators**

Indicators are weak organic acids or bases that change color depending on the acidity or base of the environment and generally at a certain pH. The solution to be titrated to find the turning point for the acid-base titration participate very little. The choice of indicators for a titration is based on the expected pH for the endpoint.

## 2. EXPERIMENTAL PROCEDURE

1. Depending on whether the sample is acidic or basic, the PH value is adjusted with the help of 1 N $H_2SO_4$ or 1 N NaOH.
2. During the experiment, a PH graph is created by taking the consumption and PH values obtained.

You need to get information about the chemicals you will use in the experiment (formula, damages, etc.) and have their MSDS with you. Questions will be asked during the experiment about the information you have acquired about the chemicals you will use.

## 3. EVALUATION OF RESULTS

a. Draw titration curves.

-Titrant volume versus pH

-Volume of titrant added against ΔpH / 0.05 ml titrant

b. Determine the concentration of the hydrochloric acid solution via the titration curve.

## RESOURCES

1. Skoog, D.A., West, D.M., Holler, J.F., “Fundamentals Of Analytical Chemistry”, Seventh edition, Harcourt Brace, 189-220, (1997).
2. Erdik, E., Sarıkaya, Y., Temel Üniversite Kimyası Cilt-1 s. 332, 2005.

# COAGULATION AND FLOCCULATION (JAR TEST)

## 1. EXPERIMENT OBJECTIVE

It is to determine the most appropriate amounts of aluminum sulphate(Alum) and iron(III) sulphate, which are the coagulants used to remove the suspending substance or color in natural surface waters, the most appropriate pH, the most appropriate mixing time and intensity by jar test.

## 2. THEORY

Coagulation (coagulation) and flocculation (flocculation) are interdependent, depending on many factors such as temperature, turbidity, color, pH, alkalinity, mixing intensity and time, and chemical reagent properties used. Therefore, the most suitable coagulation dose cannot be measured from analysis of water, but can be found by dosage experiments. These experiments are called "coagulation flocculation test or jar test". Coagulation and flocculation are widely used in environmental engineering in basic processes such as chemical precipitation, dewatering. This process aims to remove suspended and dissolved solid substances from water by adding chemicals to the water. The coagulation and flocculation process mainly aims to remove the colloid substances. Colloid substances cannot come together and combine due to their various interactions with each other and with water. Coagulation process is the process of transforming these colloid substances into a structure that can be combined with each other with the help of chemical substances and forming clusters that will start to flocculate. The flocculation process, on the other hand, is the combination of coagulated particles and turning them into balls from the separable structure by precipitation from water. For the flocculation process, the water is mixed slowly.

Substances that can be used for coagulation process;

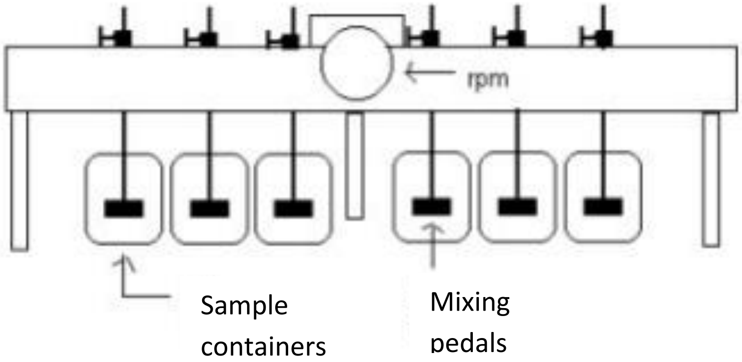
- Aluminum sulphate
- Iron (III) chloride
- Iron sulphate
- Sodium aluminate
- Ammonia aluminum sulphate

The experiment is a simulated version of wastewater treatment processes.

## 3. EXPERIMENTAL PROCEDURE

### Tools and Equipment Used

- Jar test setup



- 5 glass beaker (1 L or 500 ml)
- 2 pieces of 1 L balloon flasks
- Weighing containers
- Spectrophotometer (for turbidity test)

### Chemicals Used

Iron (III) chloride, 10%: 10 grams of Iron (III) chloride Fe($Cl_3$) is weighed and dissolved completely in some distilled water to 1L.

For pH adjustment: 1 N $H_2SO_4$, 1N NaOH is used.

### Experimental Procedure

Finding the Optimal Coagulant Dose

- 1000 ml (500 ml) water samples are placed in beakers and the samples are placed in the test setup.
- Each beaker is dosed with the specified amount of iron solution.

- After dosing, the samples are mixed rapidly for 2 minute at a speed of 100 rev/min (rpm).
- Then the samples are mixed slowly for 20-30 minutes at 30-40 rpm.
- The time passed until the formation of visible tangles, the size and appearance of the tangles are noted.
- Pedals are removed after the flocculation process. The beakers are left to settle for 30 minutes.
- After 30 minutes the sludge depths in the beakers are measured and calculated approximately. Color, turbidity and pH are measured for each dosed beaker by taking samples from the upper clear part without dispersing the precipitation.
- If the results are not sufficient, the coagulant dosage is changed and the experiment is continued until the most suitable dose is found.

Finding the optimum PH value

- By using the most appropriate dose of the coagulant used in the jar experiment in the previous section, the above procedures are repeated for the samples whose pH value is brought to 5.5, 6.5, 7.5, 8.5 and 9.5 (The pH of the samples should be adjusted before coagulant addition using 1 N $H_2SO_4$ or 1 N NaOH).
- At the end of the process, the sludge depths formed in the beakers are measured and their approximate volume is calculated. By taking a sample from the clear part, pH, color and turbidity are measured for each beaker.

## 4. CALCULATIONS

- A graph is plotted between the turbidity-coagulant dose and the reverse coagulant dose of the color.
- The change in color and turbidity according to the initial and final pH value is graphically displayed. The optimum initial pH value at the optimum coagulant dose is determined.
- The optimal mixing speed is determined by creating a graph between the coagulant dosage used and the pH (inverse of turbidity versus time).
- Then a graph is drawn between (logarithm of the inverse of the turbidity value vs. time). The line that best suits the test results is drawn and its slope is found.

## ADSORPTION

### 1. PURPOSE

In this experiment the adsorption isotherms for the adsorption of methylene blue (MB) on activated carbon will be studied.

### 2. THEORETICAL INFORMATION

Adsorption is the accumulation of a gas or liquid solute (the adsorbate) on a surface of a solid or a liquid (the adsorbent) forming a molecular or atomic film. It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. Adsorption has many applications. Its first application was probably the use of bone ashes to remove colour from syrups or alcohol. Today, adsorbent materials are widely used at water-treatment plants to remove especially organic impurities and chlorine as purification treatment.

Atoms on the surface are not wholly surrounded by other atoms and experience a bond deficiency. Thus it is generally energetically favorable for them to bond to the adsorbate.

Adsorption on solid surfaces may be either as chemisorption where a chemical band forms between the surface and the adsorbate - such as the adsorption of chloride ions on AgCl (ionic bond) or of oxygen gas on metals where oxygen to metal bonds are formed (covalent bond ) or physical adsorption results from attractions like nonpolar Vander Waals, dipole - dipole etc. The dependence of the extent of adsorption on concentration in bulk is frequently called as the "adsorption isotherm" that is, a relation that describes the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid). There are several types of isotherms describing process of adsorption, namely Freundlich isotherm, Langmuir isotherm, BET isotherm, etc.

Langmuir isotherm is applied when the adsorption occurs as a single layer (monolayer), where the following equilibrium condition is considered

$$S^{*} + M\ (g\ or\ l) \leftrightarrows S - M$$

Then the relation of the Langmuir Isotherm can be expressed as;

$$q = \frac{x}{m} = \frac{a * K * C_e}{1 + K * C_e}$$

$$1/(x/m) = 1/(a * K)(1/Ce) + (1/a)$$

Where;

**q = (x/m)** : mass of adsorbed matter per unit mass of adsorbant at equilibrium condition ( mg/g adsorbant)

**x:** concentration of adsorbed solution (mg/L)

**$C_0$:** Initial concentration of solute (mg/L)

**Ce:** concentration of solute remaining in the solution after adsorption at equilibrium condition ( mg/L)

**$K_f$:** Adsorption capacity

**n:** Langmuir constant

( Kf and n are constants related with temperature, adsorbant and adsorbate)

The plot of 1/ (x/m) vs (1/Ce) gives a straight line with a slope equal to 1/(a*K) and an intercept equal to ( 1/a).

Classical adsorption isotherm in the most general sense is the Freundlich isotherm:

$$q = \frac{x}{m} = K_f * C_e^{(\frac{1}{n})}$$

$$\log(x/m) = \log Kf + (1/n)\log Ce$$

and a plot *log (x/m)* of vs *log Ce* yields a straight line with a slope equal to *1/n* and an intercept equal to *log Kf*.

Where ;

Kf and n are Freundlich Isotherm constants.

Freundlich equation usually fails both at low and high concentrations. Freundlich isotherm is somewhat better for the adsorption from liquid solution and Langmuir equation gives better results for adsorption of gases.

Neither Freundlich or Langmuir expressions, however, are adequate for adsorption of vapors on porous solids at high vapor pressures: which is assumed to yield multi-molecular adsorption layers, and the Brauner - Emmett - Teller (B.E.T.) semi - empirical isotherm is applied in such a case, which will not be discussed here.

We will prepare our methylene blue (MB) – activated sludge isotherm by allowing MB solutions of a given concentration to equilibrate with various masses of activated carbon The amount of MB not adsorbed to the charcoal will be determined by spectophotometric method.

This will allow us to easily determine the amount of MB that has adsorbed to a given mass of the activated carbon.

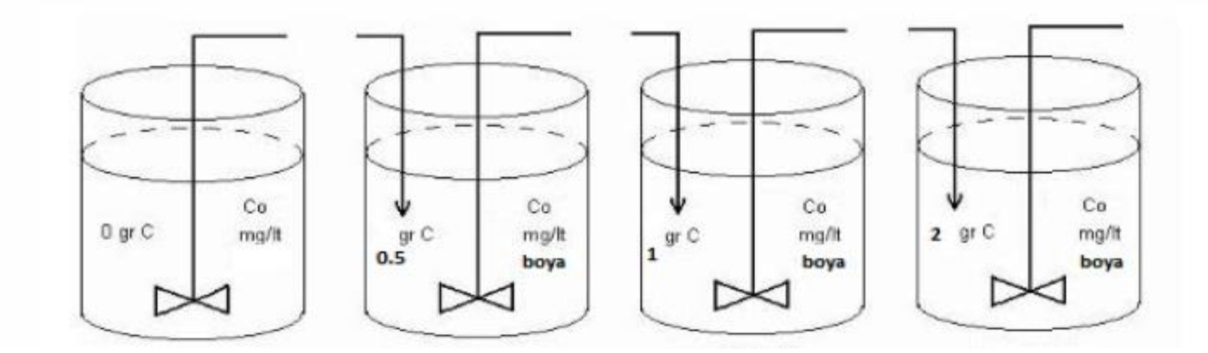
## 3. APPARATUS AND CHEMICALS

### 3.1.Apparatus

- Erlenmayer,
- graduated cylinder,
- pipette,
- filter paper,
- funnel,
- stirring rod,
- 500 mL beaker
- spectrophotometer
- pHmeter
- centrifuge

### 3.2.Chemicals

- charcoal,
- methylen blue
- 0.1M NaOH,
- distilled water.



Sample 1 Sample 2 Sample 3 Sample 4

## 4. PROCEDURE

Methylene Blue (MB , chemical formula, $C_{16}H_{18}N_3ClS$, and molecular weight 319.85 g mol$^{-1}$) is used as an adsorbate .

A stock solution of MB dye is prepared 1000 mg L$^{-1}$ by dissolving the required amount of dye powder in distilled water.

All working solutions of the desired concentrations are prepared by diluting the stock solution with distilled water.

All working solutions of the desired concentrations are prepared by diluting the stock solution with distilled water. 100mg/l concentration of working solution will be used in all the flasks in this experiment.

Adsorption equilibrium and kinetics are determined by the batch method.

Adsorption isotherms are performed in a series of 250 mL conical flasks where MB solutions with equal initial concentrations of 125 mL at pH 6.5.

Different masses of activated carbon (0, 0.5,1, 2 g) are added to MB solutions.

The flasks are shaked with an agitation of 150 rpm for 200 min to ensure establishment of equilibrium.

Samples are taken from each flask with different mass of activated carbon and centrifuged at determined intervals (i.e. 30 min., 60 min. 90,min, 120 min., 180 min, 200 min)

Follwing table should be applied for each flask with different AC mass (i.e. 0g, 0.5 g, 1 g and 2 g.)

| **Sample** | **Time (min)** | **Initial Molarity of Methylene Blue (mg/L)** | **Aliquot for anlysis (mL)** |
|---|---|---|---|
| **1** | **30** | **100** | **10** |
| **2** | **60** | **100** | **10** |
| **3** | **90** | **100** | **10** |
| **4** | **120** | **100** | **25** |
| **5** | **180** | **100** | **25** |
| **6** | **200** | **100** | **25** |

Langmuir and Freundlich isotherms are plotted using the obtained data.

Equations and isotherm constants are calculated

Activated carbon was separated from the samples by centrifugation at 3500 rpm for 10 min.

Residual concentration of MB was determined spectrophotometrically at 668 nm.

The percentage removal of MB from solution was calculated by the following:

% Removal = $((C_0-C_t)/C_0)$ *100

where $C_0$ and $Ct$ (mg $L^{-1}$) are the initial dye concentration and concentration at time $t$, respectively.

The amount of adsorbed MB onto activated carbon is calculated in terms of concentration decrease / gram of activated carbon.

Langmuir and Freundlich isotherms are plotted using the obtained data.

Equations and isotherm constants are calculated

## 5. TREATMENT OF DATA

1. Using your titration data, for each sample:

Calculate the number of moles of acetic acid in the solution before adsorption.

Calculate the number of moles of acetic acid in the solution after adsorption.

2. Determine (millimoles of MB /grams of AC) for each sample.

3. Plot the Langmuir isotherm and determine the Langmuir parameters X max and K.

4. Make the suggested plot to determine the Freundlich parameters k and n.

## 6. CALCULATIONS

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Time (min) | | | | | | | |
| Concentration (mg/L) | | | | | | | |

| MB concentration (mg/L) | Calculated q (mol/g activated carbon) | 1/Ce | 1/q | Log Ce | Logq |
|---|---|---|---|---|---|
| | | | | | |
| | | | | | |
| | | | | | |
| | | | | | |
| | | | | | |

| Langmuir Isotherm | | | | Freundlich Isotherm | | | |
|---|---|---|---|---|---|---|---|
| Equation of the curve | $R^2$ | K | a | Equation of the curve | $R^2$ | K | n |
| | | | | | | | |

## 7. QUESTIONS

1. Why did you use activated carbon as an adsorbent?

2. Which isotherm is more suitable? Why?