APPENDIX-I

CHEMICAL OXYGEN DEMAND

EXPERIMENTAL PROCEDURE

Chemical oxygen demand (COD) is the measure of oxygen consumed during the oxidation of the oxidizable organic matter by a strong oxidizing agent. Potassium dichromate (K₂Cr₂O₇) in the presence of H₂SO₄ is used as oxidizing agent in the determination of COD.

PRINCIPLE

The sample is refluxed with K₂Cr₂O₇ and H₂SO₄ in the presence of mercuric sulphate to neutralize the effects of chloride and silver sulphate, which acts as catalyst. The excess of K₂Cr₂O₇ is titrated against standard ferrous ammonium sulphate (FAS) using ferroin indicator.

The amount of K₂Cr₂O₇ used is proportional to the oxidizable organic matter present in the sample.
PROCEDURE

The round bottom flasks were rinsed with distilled water and sterilized. Then take
10ml of distilled water was taken for blank, 5ml was sample pipetted out in to the other
flasks. Each 0.3 gms of mercuric sulphate added in the flasks then added each 5ml COD
acid pipette out in to the flasks, mixed well and added each 5 ml of 0.25N potassium
dichromate solution. Then added another 10ml COD acid, mixed well. Then all these
flasks were refluxed with refluxing condenser for 2 hours. After refluxing the contents
were made up to 100ml and titrated with 0.1N ferrous ammonium sulphate [FAS]
solution using ferroin indicator. The end point is the colour changes from bluish green to
reddish brown.

When the sample was expected to have COD more than 50 mg/lit., 5ml. of 0.25 N
K₂Cr₂O₇ solutions was added to the sample. Extreme care was taken in the case of low
COD sample. Even a pinch of H₂SO₄ and Ag₂SO₄ were added. If the sample contained
chlorides in higher amount, HgSO₄ was added in the ratio of 10:1 to the chlorides. COD
could not be determined accurately, if the sample contains more than 20000 mg/lit of
chlorides.

The COD can be calculated by

\[
\text{COD} = \frac{(B-A) \times \text{Normality of FAS} \times 8 \times 1000 \times DIL.FACTOR}{\text{Volume of sample taken}}
\]
Where

A – Titre value of the sample, ml.

B – Titre value of the blank, ml.

REAGENT:

1. **K₂Cr₂O₇ solution, 0.25N.** 12.259g of dried AR grade K₂Cr₂O₇ was dissolved in distilled water to make 1lit of solution.

2. **FAS solution 0.1 N.** 39.2 g of Ferrous ammonium sulphate was dissolved in distilled water. 20 ml of concentration H₂SO₄ was added to it make 1 lit of solution. The solution was standardized with K₂Cr₂O₇ to about 100 ml of conc. H₂SO₄ was added and titrated with FAS solution using ferroin indicator.

3. **Ferroin indicator.** 0.485g of 1, 10 phenonthroline mono hydrate and 0.695 g of ferrous sulphate [FeSO₄. 7H₂O] was diluted with distilled water to make 100ml of solution.

4. **Sulphuric Acid.** H₂SO₄, concentrated [specific Gravity =11.84]

5. **Mercuric sulphate.** HgSO₄, solid.

6. **Silver sulphate.** Ag₂SO₄, solid.

7. **COD Acid.** 10.1g of silver sulphate is dissolved in 1litre of 98% concentrated sulfuric acid and kept for 24 hours with mixing.
MEASUREMENT OF pH

Electrode was washed thoroughly with distilled water and then with the sample before the measurement of pH. The system was allowed to stabilize before making the final reading.

MEASUREMENT OF ALKALINITY

Reagents
- Sodium carbonate solution,
- Sulfuric acid,
- Phenolphthalein indicator solution,
- Mixed indicator,
- Sample of dairy water.

PROCEDURE

TOTAL ALKALINITY

Added 4 drops of mixed indicator to the solution in which phenolphthalein alkalinity has been determined titrating against sulfuric acid to pH 4.5. The change was from emerald green to light pink.
PERCENTAGE OF COD REDUCTION

Percentage reduction of COD = (COD\text{ initial}-COD\text{ final}) \times 100 \over \text{COD initial}

Where,

COD initial - Initial concentration of effluent in mg/lit.

COD final - final concentration of effluent in mg/lit.

From table,

\% Reduction of COD = \frac{[1200-400]}{1200} \times 100

= 66.67\%
PERCENTAGE OF COLOUR REMOVAL

Percentage reduction of COD removal = \[
\frac{\text{COLOUR initial} - \text{COLOUR final}}{\text{COLOUR initial}} \times 100
\]

Where,

\text{COLOUR initial} - Initial absorbency.

\text{COLOUR final} - Final absorbency.

From table,

% Reduction of COLOUR removal = \[
\frac{1.211 - 0.061}{1.211} \times 100
\]

= 94.96%

CURRENT DENSITIES DETERMINATION

Current density = \frac{\text{Current}}{\text{area}} = \text{1A/dm}^2

Current = \text{Amps}

Area of the reactor cell = 4.5 \times 5.6 \times 0.8 / 100 = 0.2016 \text{ dm}^2

Applying Current = 4.5 \times 5.6 \times 0.8 \times 1 / 100 = 0.2016 \text{Amp}
Where,

- Length of the electrode = 4.5cm
- Width = 5.6cm
- Gap between electrodes = 1cm
- Current density = 1A/dm²

**DETERMINATION OF POWER CONSUMPTION**

Power consumption per Kg of COD = \( W/R \)

Where,

\[
W = V \times I \times \left( \frac{t}{1000} \right)
\]

- \( V \) - Voltage in volts
- \( I \) - Current in amps
- \( t \) - Time of electrolysis

\[
W = 12 \times 10 \times \left( \frac{7}{1000} \right)
= 0.84
\]

\[
R = [\text{COD initial} - \text{COD final}] \times \text{volume of the effluent} \times 10^{-6}
\]

\[
= [1200 - 400] \times 3 \times 10^{-6}
= 2.4 \times 10^{-3} \text{ Kg of COD removal}
\]
Power consumption = \( \frac{W}{R} \)

\[
= \frac{0.84}{2.4 \times 10^{-3}}
\]

\( = 350 \text{ Kwh/Kg of COD removal} \)

**DETERMINATION OF MASS FLUX (J)**

\[
\text{Mass flux} = \frac{[\text{COD initial} - \text{COD finial}] \times 10^{-3}}{\text{Time of operation} \times \text{Area of electrode}}
\]
DETERMINATION OF MASS TRANSFER COEFFICIENT (Cm/Sec)

In single pass reactor, (plugflow)

\[ C'_{A} \]

\[ C_{A} - dC_{A} \] \[ \Delta x \]

\[ \text{Flow rate } Q \]

Input-output + Disappearance of compound = Accumulation

At steady state

\[ QC_{A} - (C_{A} + dC_{A})Q + (-r_{A})V = 0 \]

\[ -QdC_{A} + (-r_{A})V = 0 \]

\[ (-r_{A}) = -k_{a}C_{A} \quad \text{(since } -r_{A} = -r_{A} \cdot C_{A}) \]

\[ -QdC_{A} = k_{a}C_{A}A_{C} \cdot dx \]

\[ \int_{C_{A}}^{C'_{A}} \frac{dC_{A}}{C_{A}} = \frac{k_{a}A_{C}}{Q} \int_{0}^{L} dx \]
\[-\ln \frac{C'_A}{C_A} = \frac{k_a A_c L}{Q}\]
\[-\ln \frac{C'_A}{C_A} = k x \frac{A}{Q} \quad \text{(since } k_{aL} = k)\]

\[
\frac{Q}{\text{COD}_{\text{final}}} \quad \text{Masstransfer co-efficient (k)} = \quad \ln \quad \frac{A}{\text{COD}_{\text{initial}}}\]

Where Q-Flow rate (V/Time)
A –is the active electrode area (Jd²)
APPENDIX-III

ONCE THROUGH METHOD COD VALUES

INITIAL COD - 1264 ppm

<table>
<thead>
<tr>
<th>Current (A)</th>
<th>Voltage (V)</th>
<th>10lph COD (ppm)</th>
<th>%COD Reduction</th>
<th>10lph COD (ppm)</th>
<th>%COD Reduction</th>
<th>20lph COD (ppm)</th>
<th>%COD Reduction</th>
<th>20lph COD (ppm)</th>
<th>%COD Reduction</th>
<th>30lph COD (ppm)</th>
<th>%COD Reduction</th>
<th>30lph COD (ppm)</th>
<th>%COD Reduction</th>
<th>40lph COD (ppm)</th>
<th>%COD Reduction</th>
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ABSORBANCE VALUES

INITIAL ABSORBANCE -30.6

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</table>
IONIC STRENGTH

The ionic strength, $I$, of a solution is a function of the concentration of all ions present in a solution.

$$I_c = \frac{1}{2} \sum_{B=1}^{n} c_B z_B^2$$

Where $c_B$ is the concentration of ion $B$, $z_B$ is the charge number of that ion, and the sum is taken over all ions in the solution. For a 1:1 electrolyte such as sodium chloride, the ionic strength is equal to the concentration, but for MgSO$_4$ the ionic strength is four times higher. Generally multivalent ions contribute strongly to the ionic strength.

Because in non-ideal solutions volumes are no longer strictly additive it is often preferable to work with molality rather than amount concentration. In that case, ionic strength is defined as:

$$I_m = \frac{1}{2} \sum_{B=1}^{n} m_B z_B^2$$
IMPORTANCE

The ionic strength plays a central role in the Debye-Hückel theory that describes the strong deviations from ideality typically encountered in ionic solutions. It is also important for the description of colloids. That is, the Debye length, which is the inverse of the Debye parameter \(-\kappa\), is inversely proportional to the square root of the ionic strength. Increasing the concentration or valence of the counterions compresses the double layer and increases the potential gradient.

IONIC REPLACEMENT

In the study of solution reaction kinetics it is often desirable to change the concentration of an active species without changing the ionic strength, because the latter affects the value of the rate constant \(k\). This can often be done by replacement. If for example, the \([S_2O_8^{2-}]\) is to be lowered, the solution is diluted with a solution containing the same concentration of a non-active species of equal charge e.g. \(SO_4^{2-}\) rather than just solvent. This produces a solution with a lower \([S_2O_8^{2-}]\) but of the same ionic strength.

IONIC STRENGTH AND ACTIVITY COEFFICIENTS

As it was already signaled in the introduction, all calculations done using concentrations are wrong. Ions are charged so they interact in the solution attracting and repelling each other with coulomb forces. These interactions influence ions behavior and doesn't allow to treat every ion in the solution independently. Whole phenomenon - although investigated for over 100 years - is still not fully understood and described. To be precise in our equilibrium calculations instead of using concentrations we should use
ions activities. Activities are not a theoretical construct - they can be measured for every solution. In fact whenever you put pH electrode into solution you are measuring not $[H^+]$ but activity of $H^+$ ions. It is enough to add inert salt to the solution of known acid to observe pH change that confirms activity concept (and is in accordance with results of calculations presented below).

Most popular method used to calculate ions activities is the one proposed by Debye and Huckel in 1923.

First step in calculations is calculation of so called ionic strength, using following formula:

$$ I = \frac{1}{2} \sum C_i z_i^2 $$

where $C_i$ is a concentration of $i$th ion present in the solution and $z_i$ is its charge.

Summation is done for all charged molecules present in the solution.

Second step is calculation of activity coefficients given by formula:

$$ \log f_z = -0.51 \frac{z^2 \sqrt{I}}{1 + \sqrt{I}} $$
Activity coefficient for all ions bearing the same charge is identical (although there exists slightly more precise formula in which activity coefficient is also a function of ion radius).

And now the most important thing. Activity of any ion (with charge z) is

\[ a_{ion} = f_z C_{ion} \]

Where \( f_z \) denotes activity coefficient for z-charged ions.

Equilibrium calculations made using this approach give good results for ionic strength lower than 0.1.

In all reaction quotients used throughout all sections we should replace concentrations of all ions with their activities. Mass and charge balances should use analytical concentrations of ions.

What error are we making neglecting ionic strength of the solution? Activity coefficients are relatively high for the molecules with higher charge, so let's check what will happen in the solution containing \( PO_4^{3-} \) ions. Using pH calculator you can check what will be the pH of the \( PO_4^{3-}/HPO_4^{2-} \) buffer - enter 0.02M as concentration of phosphoric acid and 0.05M as concentration of NaOH. When the ionic strength is ignored calculated pH = 11.75. When ionic strength is calculated, pH = 11.44. That's 0.31 pH unit difference.
As the activity of ions are function of their concentrations (through ionic strength), calculations have to be done iteratively. In first step you should calculate all concentrations assuming ionic strength of 0 (and all activity coefficients of 1). If some of the reagents obviously dissociated you may already calculate first value of the ionic strength at this stage. After concentrations are known you should use formulas 3 and 4 to find ionic strength and all activity coefficients and repeat calculations using these values. This gives new set of concentrations and whole process should be repeated until a result of calculations doesn’t change (or the difference between two steps or calculations is small enough). Remember, that ionic strength is calculated as sum of concentrations, not activities of ions.

**SELECTIVITY COEFFICIENT (IN ION EXCHANGE CHROMATOGRAPHY), $k_{A/B}$**

The equilibrium coefficient obtained by application of the law of mass action to ion exchange and characterizing quantitatively the ability of an ion exchanger to select one of two ions present in the same solution. The ions involved in the exchange should be specified as subscripts.
Examples:

Exchange: \(\text{Mg}^{2+} - \text{Ca}^{2+}\)

\[
k_{\text{Mg/Ca}} = \frac{[\text{Mg}]_S/[\text{Ca}]_S}{[\text{Mg}]_M/[\text{Ca}]_M}
\]

Exchange: \(\text{SO}_4^{2+} - \text{Cl}^-\)

\[
k_{\text{SO}_4/\text{Cl}} = \frac{[\text{SO}_4]_S/[\text{Cl}]_S^2}{[\text{SO}_4]_M/[\text{Cl}]_M^2}
\]

In the above equations subscript \(S\) refers to the ion exchanger ('stationary phase') and \(M\) to the external solution ('mobile phase'). For exchanges involving counter-ions differing in their charges, the numerical value of \(k_{A/B}\) depends on the choice of the concentration scales in the ion exchanger and the external solution (molal scale, molar scale, mole fraction scale, etc.). Concentration units must be clearly stated for an exchange of ions of differing charges. The corrected selectivity coefficient \((k_{A/B})\) is calculated in a way identical to the selectivity coefficient except that the concentrations in the external solutions are replaced by activities. This term should not be used as a synonym for separation factor.

**CONDUCTIVITY**

Conductivity of a substance is defined as 'the ability or power to conduct or transmit heat, electricity, or sound'. Its units are Siemens per meter \([\text{S/m}]\) in SI and micromhos per centimeter \([\text{mmho/cm}]\) in U.S. customary units. Its symbol is \(\kappa\) or \(\sigma\).
ELECTRICAL CONDUCTIVITY (EC)

An electrical current results from the motion of electrically charged particles in response to forces that act on them from an electrically applied electric field. Within most solid materials a current arise from the flow of electrons, which is called electronic conduction. In all conductors, semiconductors, and many insulated materials only electronic conduction exists, and the electrical conductivity is strongly dependant on the number of electrons available to participate to the conduction process. Most metals are extremely good conductors of electricity, because of the large number of free electrons that can be excited in an empty and available energy state.

In water and ionic materials or fluids a net motion of charged ions can occur. This phenomenon produces an electric current and is called ionic conduction.

Electrical conductivity is defined as the ratio between the current density ($J$) and the electric field intensity ($\varepsilon$) and it is the opposite of the resistivity ($\rho$, $[\Omega \cdot m]$):

$$\sigma = \frac{J}{\varepsilon} = \frac{1}{\rho}$$

Silver has the highest conductivity of any metals: $63 \times 10^6$ S/m.

WATER CONDUCTIVITY

Pure water is not a good conductor of electricity. Ordinary distilled water in equilibrium with carbon dioxide of the air has a conductivity of about $10 \times 10^{-6} \Omega^{-1} \cdot m^{-1}$ (20 dS/m). Because the electrical current is transported by the ions in solution, the
conductivity increases as the concentration of ions increases. Thus conductivity increases as water dissolved ionic species.

Typical conductivity of waters:

- Ultra pure water: $5.5 \times 10^{-6} \, \text{S/m}$
- Drinking water: $0.005 - 0.05 \, \text{S/m}$
- Sea water: $5 \, \text{S/m}$

**ELECTRICAL CONDUCTIVITY AND TDS**

TDS or Total Dissolved Solids is a measure of the total ions in solution. EC is actually a measure of the ionic activity of a solution in term of its capacity to transmit current. In dilute solution TDS and EC are reasonably comparable and the TDS of a water sample based on the measured EC value can be calculated using the following equation:

$$\text{TDS (mg/l)} = 0.5 \times \text{EC (dS/m or mmho/com)} \quad \text{or} \quad 0.5 \times 1000 \times \text{EC (\mu S/cm)}$$

The above relationship can also be used to check the acceptability of water chemical analyses. It does not apply to raw wastewater or high-strength industrial wastewater. As the solution become more concentrated (TDS > 1000 mg/l, EC > 2000 \mu S/cm), the proximity of the solution ions to each other depresses their activity and consequently their ability to transmit current, although the physical amount of dissolved solids is not affected. At high TDS values, the ratio TDS/EC increases and the relationship tends toward $\text{TDS} = 0.9 \times \text{EC}$. 
In these cases the above-mentioned relationship should not be used and each sample should be characterized separately. For water for agricultural and irrigation purpose the values for EC and TDS are related to each other and can be converted with an accuracy of about 10% using the following equation:

\[
TDS \text{ (mg/l)} = 640 \times EC \text{ (ds/m or mmho/cm)}.
\]