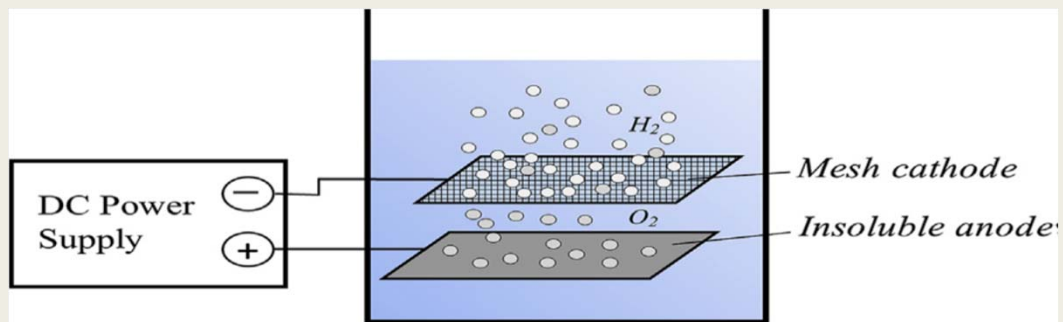


ELECTROFLOTATION

CEE 597T
Electrochemical Water and Wastewater Treatment

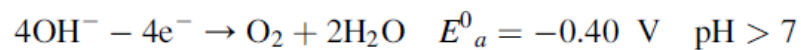


- EF is a physical chemical method of water treatment from insoluble (dispersed) substances.
- The method is based on conducting the water electrolysis on insoluble electrodes and flotation effect. While carrying out the water electrolysis, gas bubbles of oxygen and hydrogen are generated at the anode and cathode, respectively.
- When gas bubbles rise up to the liquid surface due to the density difference between gas and liquid phases, they are faced with dispersed particles of pollution, adhere to them and float them to the water surface to form a stable flotsludge layer, which is later removed by skimmers or other mechanical devices.
- Nevertheless, the formation of both hydrogen and oxygen gas bubbles hydrogen bubbles produced at the cathode play the main role in the flotation process.

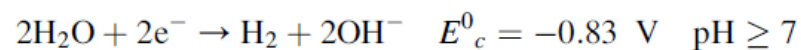
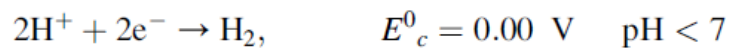
- EF process is a complex process, which can be described through the following steps:
 - Electrochemical generation of gas bubbles
 - Interaction of dispersed particles with gas bubbles and formation “particle-gas bubbles” flotocomplexes
 - Flotation of formed complexes to the water-air interface and formation of the froth layer (flotosludge)

- Usually high removal efficiency from dissolved compounds can be achieved with the optimum concentration of dissolved pollutants in wastewater in the range between 10 and 100 mg/L and the maximum concentration below 200 mg/L

At anode:



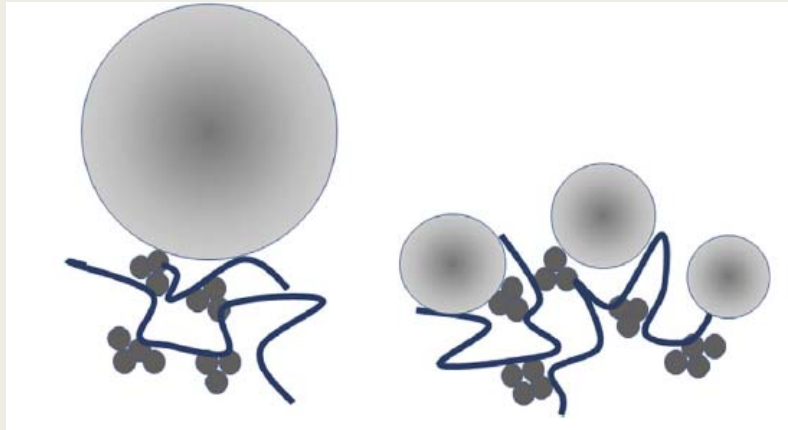
At cathode:



The Theory of Flotation

- Flotation phenomenon is associated with the phenomena of wetting and nonwetting of particles by water. The better the wetting of particles by water is, the worse the adhesion of particles to gas bubbles.
- The ratio between particle and gas bubble size influences significantly the efficiency of flotation because it determines the efficiency of the collision and the subsequent attraction.
- There is a critical particle size for a particular gas bubble size below which collision between gas bubbles and particles do not occur.
- On the contrary, very small particles have low weight and move along with water current, thus flowing around the popping up gas bubbles
- The larger particles increase the probability of the “bubble-particle” complex formation. In this regard in real applications flotation is often preceded by coagulation (destabilization of colloids) and flocculation (aggregation of destabilized particles under the influence of high-molecular compounds or flocculants) processes.
- In general dispersed particles and flocs can be floated by either one larger or few smaller gas bubbles.

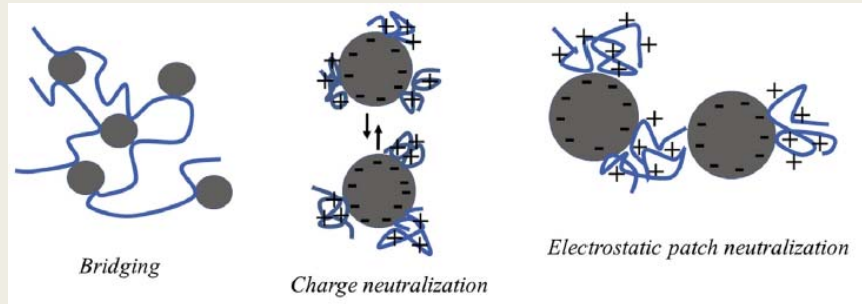
Different ways of pollutants flotation by gas bubbles of different size



The larger particles increase the probability of the “bubble-particle” complex formation. In this regard in real applications flotation is often preceded by coagulation (destabilization of colloids) and flocculation (aggregation of destabilized particles under the influence of high-molecular compounds or flocculants) processes. In general dispersed particles and flocs can be floated by either one larger or few smaller gas bubbles.

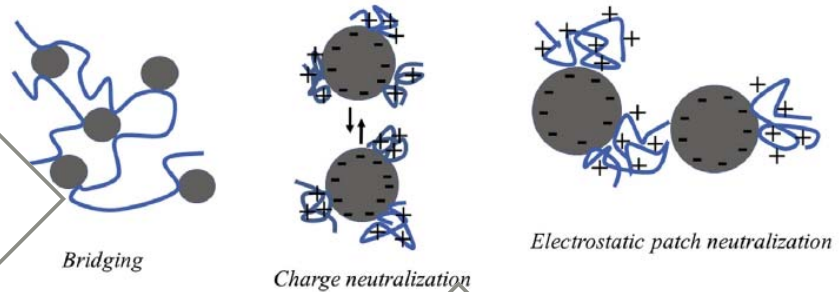
- The mechanism of flocculant action is that large flocs having good sedimentation properties are formed between flocculant and dispersed particles. The formation of flocs occurs because of the adsorption of flocculant molecule on the surface of particles, which can take place by three different mechanisms. They are charge neutralization, electrostatic patch, and bridging flocculation.

Mechanism of flocs formation.



The bridging mechanism of floc formation is typical for high-molecular-weight nonionic flocculants, occurs most frequently and includes the simultaneous adsorption of flocculant molecule on the surface of few particles leading to the formation of polymer bridges between them

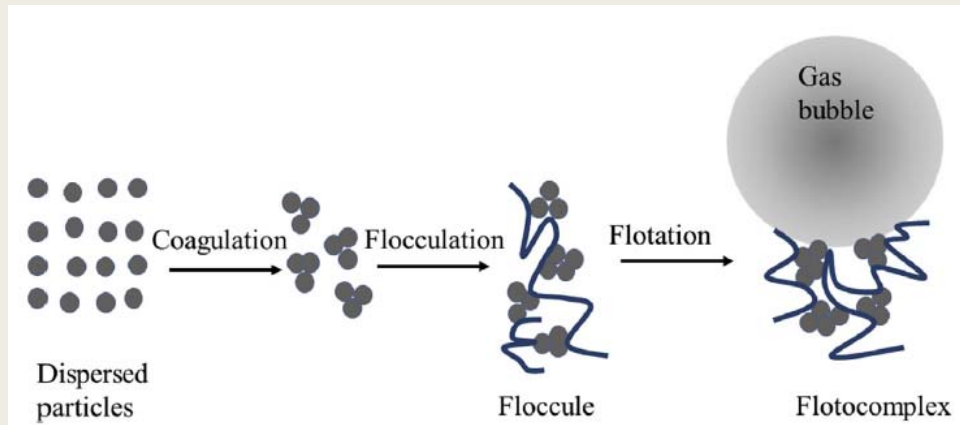
The bridging mechanism of flocculation is considered to have the strongest bonds followed by the electrostatic patch neutralization and charge neutralization mechanism having the weakest flocculants/particles bond.



The mechanism of charge neutralization leads to adhesion of particles because of the decrease of electrostatic repulsion that takes place when oppositely charged molecules of flocculants are adsorbed on particle surface, thus neutralizing its charge. This mechanism is typical for flocculants of low molecular weight (around 104).

Mechanism of electrostatic patch neutralization takes place in the case of particles with low-density charge and flocculants of high density charge. In that case polymer flocculant can electrostatically bond to and neutralize few oppositely -charged particles.

The sequence of water treatment steps often combined with flotation



- Equations demonstrates that the amount of hydrogen gas generated is twice that of oxygen gas. The gas generating rate can be calculated according to the Faraday's Law

- $$Q_H = \frac{IV_0}{n_H F}$$

- $$Q_O = \frac{IV_0}{n_O F}$$

Where Q_H is the hydrogen gas generating rate (L/s) at the normal state;

Q_O the oxygen gas generating rate (L/s) at the normal state;

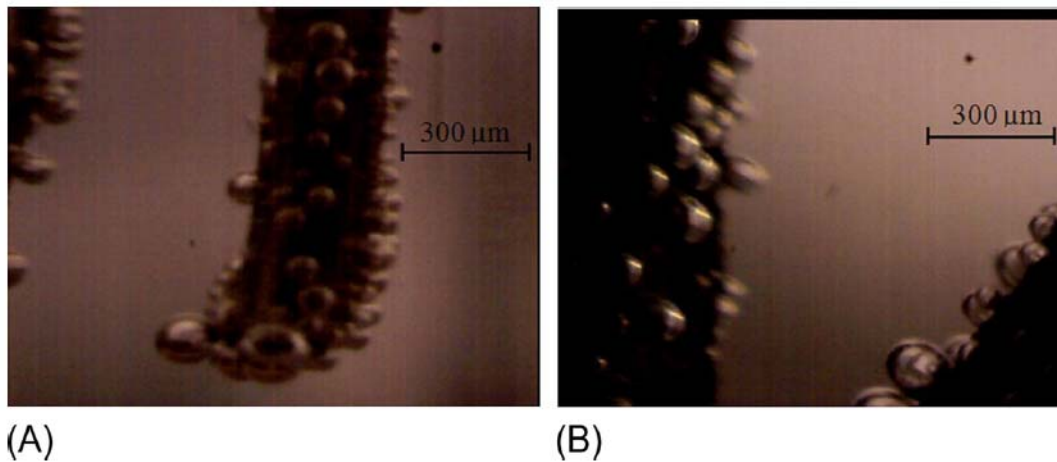
V_0 the normal volume of gases at the normal state (22,4L/mol);

F the Faraday's constant (96,500 C/molelectrons);

n_H the electrons transfer number of H_2 (2 mol electrons per mole of H_2); and

n_O is the electrons transfer number of O_2 (4 mol electrons per mole of O_2).

$$Q_g = Q_H + Q_O = \frac{IV_0}{F} \left(\frac{1}{n_H} + \frac{1}{n_O} \right) = 1.74 \times 10^{-4} I$$



- Image of the hydrogen bubbles formed on the stainless-steel cathode (A) and of the oxygen bubbles formed on the anode (B), with a cell potential of 3.5 V, pH 7, and 0.1 mol L⁻¹ NaCl solution. Images obtained by laser diffraction.

The advantages of EF are

- i. the ability to conduct the process without additional chemicals. However, reagents may only be used for the formation of precipitation and their flocculation, which allows separation of fine particles including ions (ion flotation).
- ii. high dispersion of bubbles in the range of microns and tens of microns, which is up to two orders of magnitude smaller than in the conventional froth flotation.
- iii. electrodes can be arranged to offer total coverage of the flotation tank surface, avoiding bypass;
- iv. the electric field gradient between the electrodes helps on flocculation and flotation even in the presence of surfactant;
- v. the gas evolution, flotation time, and other operational conditions can be rapidly checked and are relatively easy to control;
- vi. ionic charge of the effluent is not a crucial variable, as is seen in DAF
- vii. Simultaneous aeration of wastewater during EF allows simultaneous decomposition of easily oxidizable substances and microorganisms.
- viii. the ability to significantly accelerate the process of sedimentation and separation of precipitates, which takes 2-6 h in conventional chemical processes.
- ix. Flotosludge formed during EF is of high density comparable to traditional froth flotation where water content in the froth layer can be up to 10%. This allows reducing the water loss.

EF is used mainly for the removal of

- *metal ions;
- *fine-dispersion metal hydroxides such as iron, copper, nickel, cadmium, chromium, magnesium, etc.;
- *suspended solids;
- * phosphates;
- * suspensions;
- *resinous and emulsified substances;
- *mineral and industrial oils; and
- *grease and surfactants from industrial wastewaters.

Bubble Size Influencing Factors

- The very fine bubbles produced improve the EF process, because the fine particles float easier with small bubbles and the smaller bubbles provide larger surface area for particle attachment.
- In general, the bubbles formed during conventional flotation process present an average diameter from 0.9 to 2.0 mm, whereas bubbles formed during the EF process range from 8 to 15 μm , being therefore more homogeneous in size.
- As the bubble size decreases, the probability of particle-bubble collision (and hence flotation separation) increases.

- The size of gas bubbles depends on
 - the conductivity of the wastewater, i.e., **the lower the electrical conductivity of water, the higher the electric field strength and the bubbles are smaller.**
 - the properties of the electrode surface,
 - the shape of electrodes,
 - pH and temperature of the medium,
 - the surface tension at the electrode-solution interface, and
 - the current density.
- **In general the size of gas bubbles formed during EF is smaller than those in conventional flotation methods.**
- **The size of hydrogen bubbles is about twice smaller than oxygen bubbles evolved at the anode. The diameter of hydrogen bubbles in EF varies from 20 to 40 μm .**
- Among these parameters, the most important is the electrode material and its position in the electrochemical cell, which plays an important role in the size of bubbles.

Operating Parameters

A significant part of the *electric energy losses* occurs while overcoming resistance of the electrolyte and overpotentials at the electrodes, which depends on

- *the electrode material,
- *their surface state,
- *current density,
- *solution temperature, and other factors.

- EF allows achieving high-pollutant removal efficiencies reaching up to 99% within only 5-10 min of process operation.
- The efficiency of the EF (%) depends on many parameters such as
 - *applied current density,
 - *material of anodes,
 - *acidity and composition of the medium,
 - *size of bubbles and
 - *dispersed particles and their surface charge,
 - *arrangement of electrodes inside
 - *electroflotator (equipment used for carrying out of the EF process),
 - *solution flow rate, etc.

Electrode Material

- The material of electrodes used in EF process influences the amount of produced gas bubbles. Such *anodes with high overvoltage toward OER* and *cathodes with a high overvoltage toward hydrogen evolution* reactions *produce fewer bubbles* at the applied potential difference or applied current compared to the electrodes with a lower overvoltage toward hydrogen and OERs.
- There are different cathode materials, which are used in EF. They are, for example, graphite- and carbon-based electrodes, MMO electrodes, stainless steel cathodes, copper, nickel, etc. The most commonly used cathodes are made of stainless steel because of its low cost, stability, and high performance toward hydrogen gas allocation.
- *The lower the cathode overvoltage toward hydrogen evolution is, the smaller bubbles of hydrogen (range of nanometers) are formed. Consequently higher overvoltage leads to the formation of larger hydrogen bubbles.*
- Anodes can be either insoluble like MMO electrodes or soluble made of aluminum and iron in the case if EF is enhanced by electrocoagulation process.

- While using *soluble iron or aluminum electrodes*, along with gas generation, there is a dissolution of iron and aluminum cations forming metal hydroxides, which trap dispersed particles of pollutants and coagulate. Limited distance between electrodes and significant sizes of coagulating flocs allow good adhesion of gas bubbles to the flocs.
- When using *insoluble anodes*, electrophoresis (movement of dispersed particles under the influence of external electric field), discharge of particles at the electrode surface, and presence of compounds able to deplete particle solvation layer affect strongly the efficiency of EF.
- The use of insoluble electrodes is usually favorable at low particles concentration, whereas soluble electrodes show better performance in the case of high concentrations of stable pollutants resistant to aggregation.

Cathodes

- For the EF process, hydrogen bubble generation has a fundamental role; therefore, cathodic materials, usually metals, are selected for the promotion of a hydrogen evolution reaction.
- The most common material used as cathodes in EF is stainless steel, chosen for its low cost and availability.
- However, other electrodes can also be applied, such as nickel, which presents low overpotential for a hydrogen evolution reaction, leading to lower energy consumption.
- Other material commonly applied is titanium, which is highly stable and thus is selected as a cathode material for cases of corrosive effluents.
- Additionally, some studies combining electrocoagulation-electroflotation (ECEf) have applied aluminum and iron.

Anodes

- Lifetime and low overpotential for oxygen evolution reaction (OER) are the most important properties for anodes.
- Graphite, PbO_2 , and Pt are insoluble anodes most commonly used in EF.
- However, each of these presents certain limitations, such as:
 - *graphite* anodes present *low durability*;
 - *lead dioxide* anodes are also cheap and of easy fabrication but present *high oxygen evolution overpotential* and consequently low electroactivity for OER;
 - PbO_2 can potentially *generate Pb^{2+} species* which are highly toxic, producing a secondary source of pollution; and,
 - *platinum* anodes are much more stable than lead or graphite electrodes, also presenting a low OER overpotential, but their *high cost* is a burden for their industrial application.
- *dimensionally stable anodes (DSA)*, a new class of highly stable electrodes with high electroactivity for oxygen production was achieved which enabled industrial application of EF. Normally, the DSA coating is composed of a metallic oxide (such as RuO_2 and IrO_2), due to its high electrocatalytic activity, and by non-conductive metallic oxides (TiO_2 , Ta_2O_5 , ZrO_2 , Nb_2O_5 , etc.), which form a solution to recover the metallic support (Ti, Ta, Zr, W, Nb, Bi, etc.).

Increase in hydrogen bubbles



Pb, Sn, Fe, Ni, Pt



Increase in oxygen bubbles

Electrode Size

- Bubble size depends on the geometry of the electrode.
- Bubble diameter increases with increasing thickness of the wire mesh.
- The bubble diameter depends on the electrode curvature.
- The electrode surface curvature influences the distribution of hydrogen and oxygen bubbles, enabling the control of production ratio and bubble size.
- Roughness was pointed out to present strong influence on the bubble production, where rougher surfaces were able to produce a higher amount of small bubbles, which favors EF treatment efficiency. treatment efficiency
- Improvement on removal efficiency was related to the increase in electrode area, which is directly related to the generation of bubbles and electrogenerated coagulants.

Flocculants

- There are few classifications of flocculants.
- **Organic** (for example, polyethylene oxide and polyacrylamide) and
 - natural, such as starch, or
 - natural resins or synthetic ones.
 - Synthetic flocculants: classified into *nonionic* such as polyethylene oxide, polyelectrolyte [either anionic (-COOH, -PO(OH)₂, -SO₃H, etc.) or cationic (-NH, NH₂, etc.) electrolyte depending on the functional groups], and copolymers (which can comprise both cationic and/or anionic functional groups).
- **Inorganic** (for example, active silicic acid).
- The rate of floccules sedimentation is hundreds and thousands times higher than sedimentation of separate particles.
- The dose of flocculants is usually 10-fold lower than the dose of coagulants.

Current Density

- It directly affects the amount of produced gas and consequently the efficiency of pollutants removal by EF.
- *The higher the applied current density, the more gas bubbles are produced.*
- Efficiency of particles removal increases with the current density due to higher degree of saturation by gas, which lead to higher amount of successful collisions between bubbles and particles.
- *The size of produced bubbles is also dependent on the applied current density. Higher current densities should lead to smaller gas bubbles generation*, which is explained by the fact of intensive electrode reactions at higher densities, accumulation of dissolved gases at the electrode's surface, shorter time of gas bubbles nucleation, and faster growth and detachment of grown bubble from the surface of electrode.

Particle Charge

- The charge of particles is greatly dependent on the pH of solution. Interaction of similar charged particles and bubbles contributes to the electrostatic repulsion and increase of energy barrier.
- Higher efficiency of EF is obtained when countercharged bubbles and particles adhere, thus providing better formation of floc/sludge.
- For example, metal ions are charged positively. Bubbles of hydrogen and oxygen produced at the cathode and anode, respectively, have a charge at the moment of their detachment from the electrode surface. Oxygen bubbles are charged positively and hydrogen bubbles are charged negatively. Therefore, EF of metals by hydrogen bubbles provides higher metal removal efficiencies than the same process with the prevalence of oxygen bubbles.
- Consequently, efficiency of EF is higher in the case of countercharged or zero-charged gas bubbles and particles.

Liquid Medium Composition

- *The higher the concentration of particles in the flotation medium is, the higher the possibility of particles and bubbles collision, adhesion, and flotation.*
- The presence of anions in the treated solution influences the service life of the electrodes and consequently the frequency of electrode change.
- High concentration of Cl^- , SO_4^{2-} , NO_3^- , Br^- , and F^- anions starts to facilitate the corrosion of electrodes (especially steel electrode).
- The trace amount of chlorides and sulfates at concentrations as low as 1 mg/L is enough to initiate the electrodes intensive corrosion, while the concentration of the anions above 100 mg/L to the electrodes aggressive dissolution requiring the use of more expensive stable electrodes.
- On the contrary, the presence of OH^- or SiO_3^{2-} anions can form the protective layer on the electrode surface.
- It is recommended to change the polarity of electrodes occasionally to prevent the sedimentation of carbonates on the electrode surface. If the polarity change is not possible, then the deposition of carbonates can be prevented by addition of conditioning reagents such as lime or soda.

- Addition of flocculants into the treated solution usually enhances the efficiency of EF by reducing the time required for the achievement of the same removal values.
- *The higher the molecular weight of flocculants, the better enhancement of EF is achieved, which is explained by stronger trapping of flocculants to particle due to the bridging mechanism of flocs formation.*
- The presence of surfactants in the treated solution stabilizes the gas bubbles. The presence of surfactants in the treated solution stabilizes the gas bubbles preventing their coalescence and thus keeping their size in a smaller range. *The smaller the size of gas bubbles, the higher their surface area, the slower their rising speed, and as a result the greater the possibility of successful adhesion to suspended particles.*

pH of the Medium

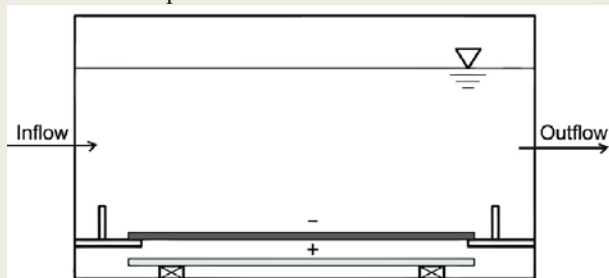
- Such that it was reported that small hydrogen bubbles of 16 μm diameter was obtained at pH 3-4 while recovering sphalerite and hydrogen bubbles with the size below 30 μm can be generated at pH of 2-6 at iron and carbon cathodes. Another study reported the opposite dependence of the smaller hydrogen bubbles generation in alkaline media (w33 μm at pH 9-12) compared to acidic one (w35-36 μm at pH 2-4) at the 316 stainless steel cathode.
- Hydrogen bubbles are larger in an acid medium (20–70 μm) than in a neutral (15–20 μm) or alkaline medium (15–30 μm). In a neutral or alkaline medium, the hydrogen bubble size is smallest indifferent of the cathode material; however, in an acid medium the cathode material influences the bubble size.
- The oxygen bubbles are larger in a neutral and alkaline medium than in an acid medium.
- For example, for platinum bubbles with 25 μm are formed in an acid medium, whereas in a neutral and alkaline medium the diameter increases to 30 and 55 μm , respectively.
- Therefore, the bubble size variation tends to follow a trend opposite to ion excess, and thus bubble size can be easily controlled by varying the pH value of the medium and the electrode materials.
- However, it is difficult to control pH inside the system due to the continuous release of OH^- and H^+ ions, where the higher the current density, the higher the changes in the pH of the system.

Reactor Designs

- The placing of electrodes is an important aspect of the EF process, since the configuration used is able to maximize the system efficiency.
- Therefore, some factors must be considered in electrode arrangement. Basically, ohmic drop and O_2 and H_2 bubble accumulation between the anode and cathode, which form a nucleus on the surface of the electrode, must be taken into account.
- These configurations should be minimized in order to guarantee that mass transfer limitations between the electrodes is the smallest possible.
- Electrodes used for EF present a series of arrangements that will be presented as: ***conventional arrangements, vertical arrangement, and open arrangements***

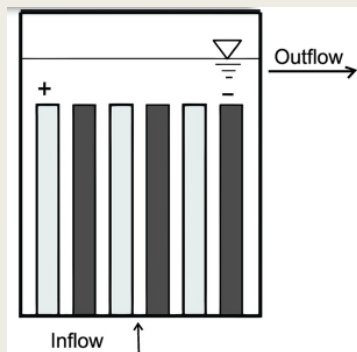
Conventional Arrangement

- In EF reactors, usually, an anode is installed at the bottom of the reactor and a cathode is fixed around 10–50 mm distant from the anode.
- However, this arrangement does not contribute for direct interaction from bubbles produced at the bottom with the effluent flow. Thus, the bubbles dispersed on the bottom electrode are not well dispersed immediately in the effluent.
- Furthermore, the potential risk of flock ruptures is also present, affecting the EF process efficiency.
- Additionally, if effluent conductivity is not adequate, a larger spacing between electrodes is necessary to avoid short-circuiting between a cathode and an anode, resulting in elevated energy consumption



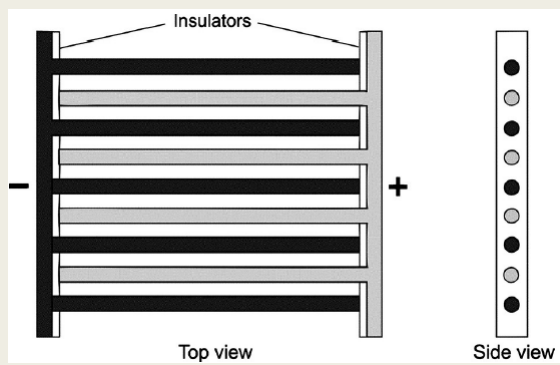
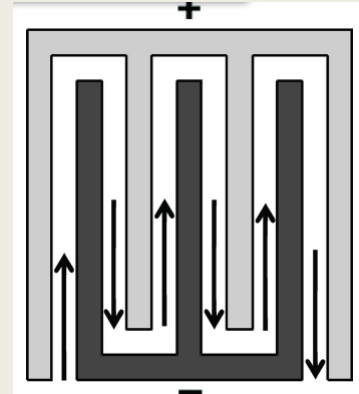
Vertical Arrangement

- Another option of electrode arrangement is by vertically arranged plates. In this configuration, electrodes are placed in parallel and in an equal distance, and therefore can be easily placed.
- Their main disadvantage is that the bubbles generated tend to rise along the electrode; consequently, a rapid coalescence is seen and undesirably big bubbles are formed, which hinders the process efficiency.

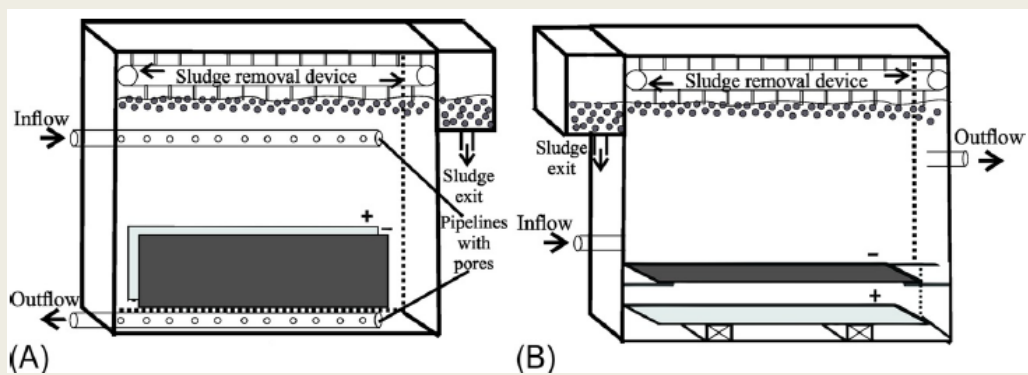


Open Arrangements

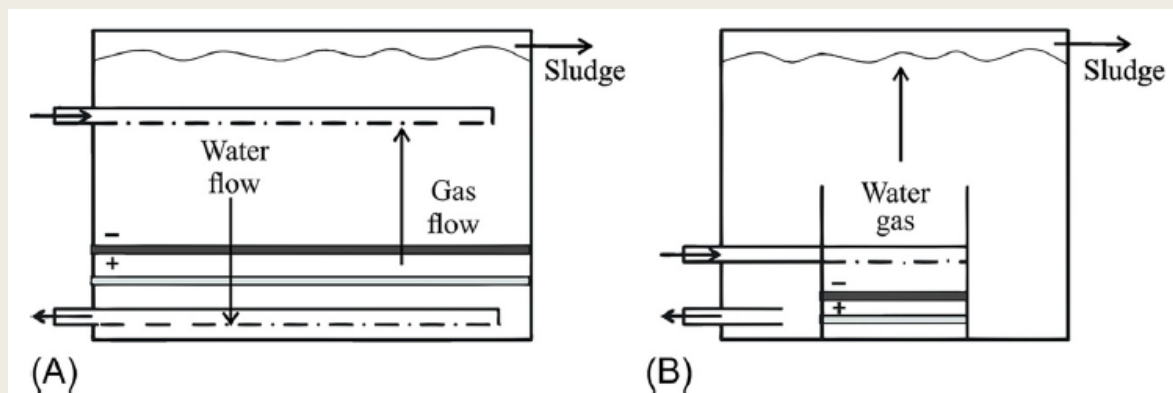
- The anode and cathode are placed in the same position; this is known as open arrangement.
- The rapid dispersion of small bubbles generated inside the effluent flow is responsible for the flotation efficiency.
- The fact that both the cathode and the anode are leveled, combined with the open configuration, leads to electrode direct interaction.
- Therefore, bubbles generated and rapidly dispersed are fixed onto the flocks with high efficiency.



One-Chamber Reactors



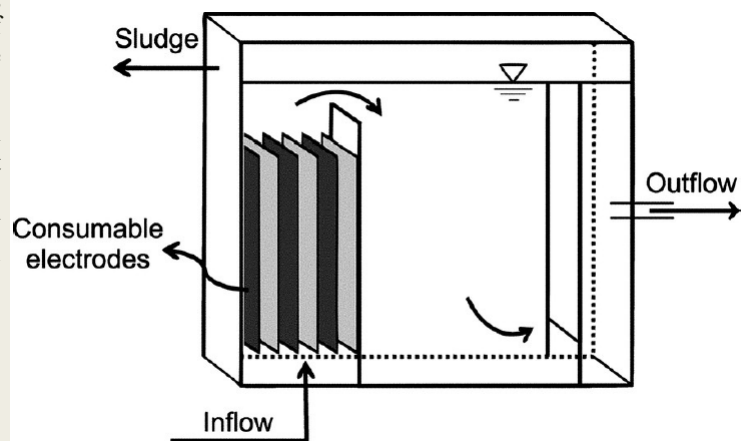
Schematic of one chamber reactor with horizontal (A) and vertical (B) flow.



- Operation modes of flow in a EF unit: counter-current (A) and co-current (B).

Two-Chamber Reactors

- In the first chamber there is a rapid formation of gas bubbles due to high current, accelerating adherence and flotation of contaminant particles up to the surface, forming foam.
- In the second chamber, the final treatment occurs where current applied is chosen in order to produce bubbles at a laminar flow regimen, propitiating the removal of suspended impurities



Water and Wastewater Treatment by Electroflotation

Summary of Main Synthetic and Real Wastewater Treatments Using EF as Innovative Treatment: Experimental Conditions and Efficiencies

Wastewater treatment with EF					
Anodes	pH conditions	Current density	Pollutant	Treatment efficiency (%)	Ref.
Al	10	350 A m ⁻²	Heavy metals	97	[6]
Ti-IrO ₂	7	150 A m ⁻²	Bitumen	92.6	[11]
Ti/IrO ₂ -Sb ₂ O ₃ -SnO ₂	5-9	2 F m ⁻²	Restaurant wastewater	84.3	[16]
Graphite-Al	7.5	1-3.6 A cm ⁻²	Emulsion and oil-bearing wastewater	94-95	[17]
PbO ₂ -Al	4.5	1.2 A	Oil-water emulsions	92	[18]
Al	7	8.42 mA cm ⁻²	Tween 20	74.79	[64]
Al	4-5	12 mA cm ⁻²	Fluor	100	[75]
Al	6-7	75 A m ⁻²	Fluor	79	[76]
Ti/IrO ₂	7.5	100 A m ⁻²	Synthetic wastewater	94	[77]
Al	5-6	43 A m ⁻²	Cafeteria wastewater	> 95	[78]
Al	8	20 V	Heavy metals	99	[80]
Al-Ti/Ru _{0.34} Ti _{0.66} O ₂	4.5	19.40 A m ⁻²	Emulsified oil	95.90	[81]
Al	5	0.5 A m ⁻²	Melanoidins	95	[86]
Al-Fe	7.5	40 mA cm ⁻²	Dyes	98	[92]
Ti-Al	6-7	2.0 A m ⁻²	Laundry wastewater	70	[95]
Al-Fe	7-11	3.2 mA cm ⁻²	Nitrate	96	[28]

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