

**CEE 597T**

**Electrochemical Water and Wastewater Treatment**

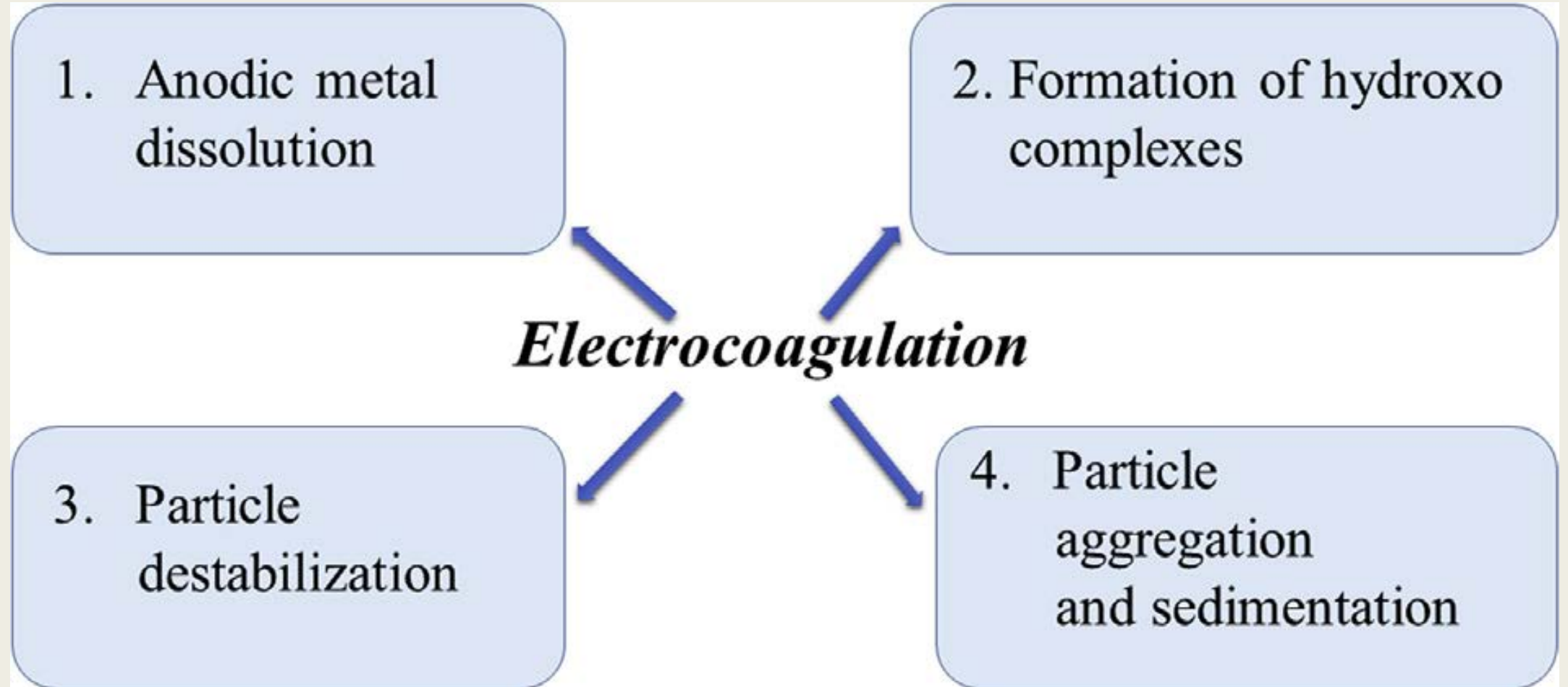
UNIT 2

ELECTROCOAGULATION

# Electrocoagulation Fundamentals

- Electrocoagulation is an electrochemical water and wastewater treatment which uses an electrochemical cell in which direct current voltage is applied to sacrificial electrodes, commonly iron or aluminum.
- EC involves the generation of coagulant in situ by dissolution of metal from the anode with simultaneous formation of hydroxyl ions and hydrogen gas at the cathode.
- This process produces the corresponding aluminum or iron hydroxides and/ or polyhydroxides, with the added benefit of the gas generated assisting in bringing the flocculated particles to the surface while providing them additional buoyancy to float at the water surface.

# Main steps of electrocoagulation



# Coagulation

Coagulation is the addition and rapid mixing of a coagulant. Result is destabilization of the colloidal and fine suspended solids, and the initial aggregation of these destabilized particles.

Flocculation is the slow stirring or gentle agitation to aggregate the destabilized particles and form a rapid settling floc. When a coagulant is added to the water, it dissociates, and the metallic ion undergoes hydrolysis and creates positively charged hydroxo-metallic ion complexes. The generalized expression for these complexes is  $Me_q(OH)_p^{z+}$ . For an aluminum salt, some of the complexes are  $Al_6(OH)_{15}^{+3}$ ,  $Al_7(OH)_{17}^{+4}$ ,  $Al_8(OH)_{20}^{+4}$ ,  $Al_{13}(OH)_{34}^{+5}$ . For an iron salt they are  $Fe_2(OH)_2^{+4}$  and  $Fe_2(OH)_4^{+5}$ . These complexes possess high positive charges and are adsorbed to the surface of the negative colloids. This causes the reduction of the zeta potential to a level where the colloids are destabilized. The destabilized particles along with complexes aggregate by interparticulate attraction due to van der Waals' forces. These forces are aided by the gentle agitation of the water.

Traditional chemical coagulation uses aluminum and iron coagulants. The most common aluminum coagulants are aluminum sulfate, aluminum chloride, and sodium aluminate. Iron coagulants include ferric sulfate, ferrous sulfate, ferric chloride, and ferric chloride sulfate.

<https://youtu.be/OYhQiaxlpt4>

<https://youtu.be/U4OQIKURnvQ>

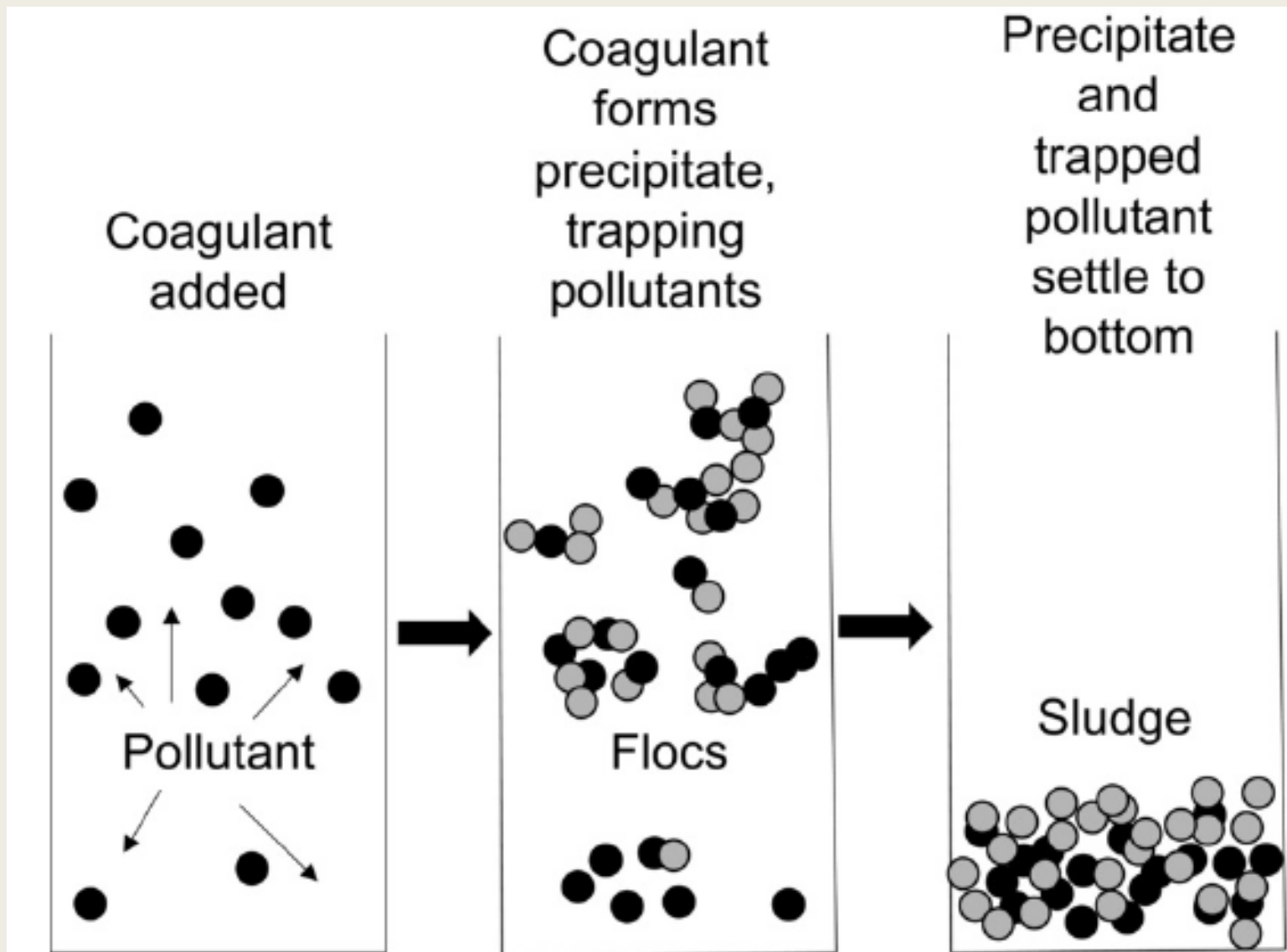


Illustration of the chemical coagulation process to remove colloidal pollutants

# Advantages of EC

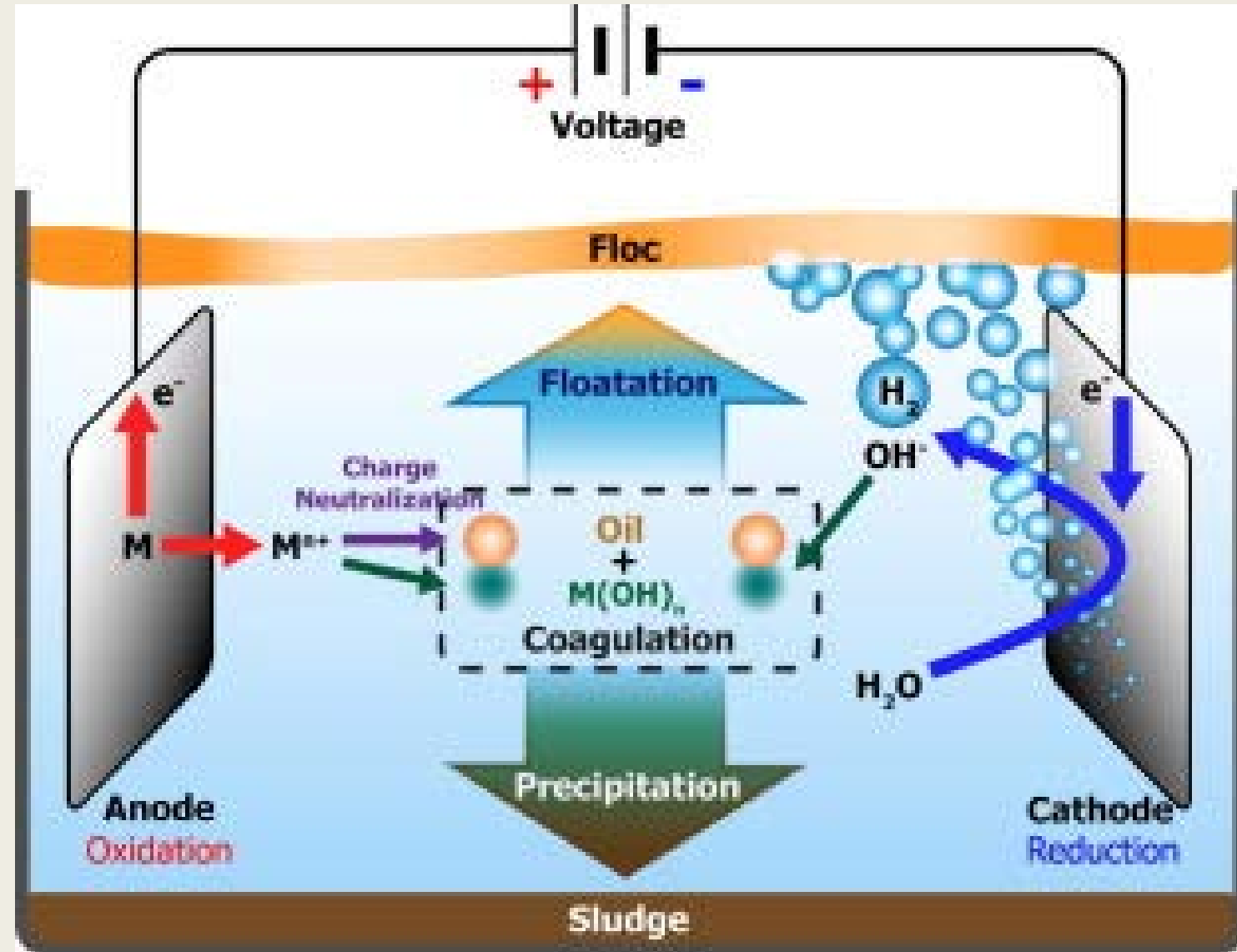
- EC requires simple equipment and is easy to operate with sufficient operational latitude to handle most problems encountered on running.
- Wastewater treated by EC gives palatable, clear, colorless and odorless water.
- Sludge formed by EC tends to be readily settleable and easy to de-water, because it is composed of mainly metallic oxides/hydroxides. Above all, it is a low sludge producing technique.
- Flocs formed by EC are similar to chemical floc, except that EC floc tends to be much larger, contains less bound water, is acid-resistant and more stable, and therefore, can be separated faster by filtration.
- EC produces effluent with less total dissolved solids (TDS) content as compared with chemical treatments. If this water is reused, the low TDS level contributes to a lower water recovery cost.
- The EC process has the advantage of removing the smallest colloidal particles, because the applied electric field sets them in faster motion, thereby facilitating the coagulation.
- The EC process avoids uses of chemicals and so there is no problem of neutralizing excess chemicals and no possibility of secondary pollution caused by chemical substances added at high concentration as when chemical coagulation of wastewater is used
- The gas bubbles produced during electrolysis can carry the pollutant to the top of the solution where it can be more easily concentrated, collected and removed.
- The electrolytic processes in the EC cell are controlled electrically and with no moving parts, thus requiring less maintenance.
- The EC technique can be conveniently used in rural areas where electricity is not available, since a solar panel attached to the unit may be sufficient to carry out the process.

# Disadvantages of EC

- The sacrificial electrodes are dissolved into wastewater streams as a result of oxidation, and need to be regularly replaced.
- The use of electricity in many places may be expensive.
- An impermeable oxide film may be formed on the cathode leading to loss of efficiency of the EC unit. However, this does not occur in a such unit for the water is forced into turbulence and this oxide is never allowed to form.
- High conductivity of the wastewater suspension is required.

# How it Works

- As water passes through the electrocoagulation cell, multiple reactions take place simultaneously.
- First, a metal ion is driven into the water.
- On the surface of the cathode, water is hydrolyzed into hydrogen gas and hydroxyl groups.
- Meanwhile, electrons flow freely to destabilize surface charges on suspended solids and emulsified oils.
- As the reaction continues, large flocs form that entrain suspended solids, heavy metals, emulsified oils and other contaminants.
- Finally, the flocs are removed from the water in downstream solids separation and filtration process steps.



[https://www.youtube.com/watch?v=v9\\_ZfL-pxl](https://www.youtube.com/watch?v=v9_ZfL-pxl)

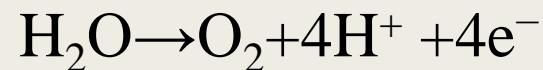


# Reactions

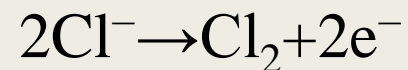
**At the anode**, metal is oxidized into cations



In this equation, Z is the number of electrons transferred in the anodic dissolution process per mole of metal. In the case of high anode potential, secondary reactions may occur. Water may be oxidized and leads to hydronium cation and oxygen gas and in the presence of chloride anions,  $Cl^{-}$  may be oxidized into  $Cl_2$ . The latter being a strong oxidant may contribute to the oxidation of dissolved organic compounds or may lead to the formation of  $ClOH$  that also plays the role of oxidizer.



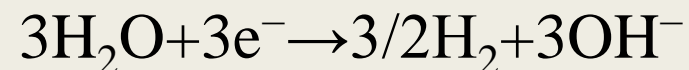
$$E^{\circ} = 1.23V/ENH$$



$$E^{\circ} = 1.36V/ENH$$

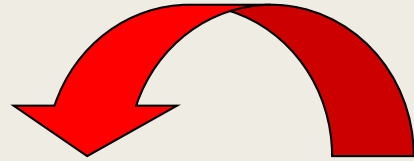


**At the cathode:** water is reduced into hydrogen gas and hydroxyl anions

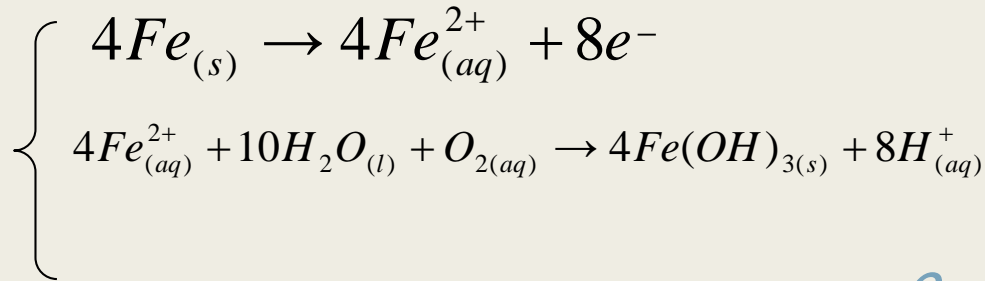


$$E^{\circ} = 0.00V/ENH$$

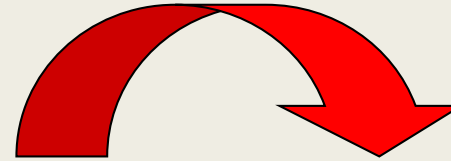
# Electrocoagulation with Iron Electrode



*Mechanism 1*

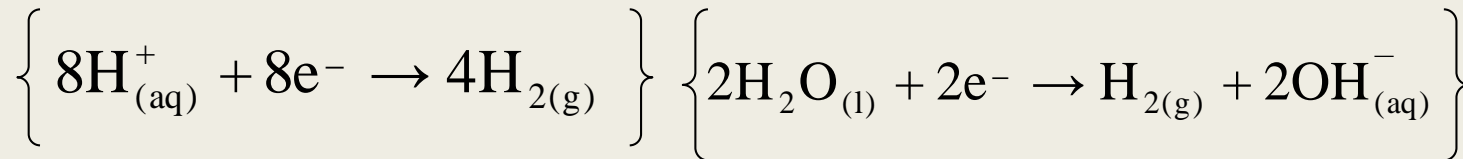
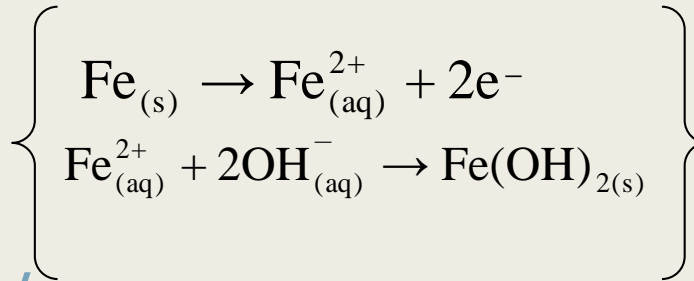


*Cathode*

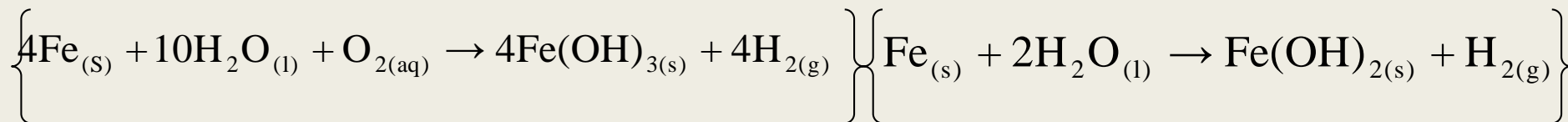


*Anode*

*Mechanism 2*



*Overall*

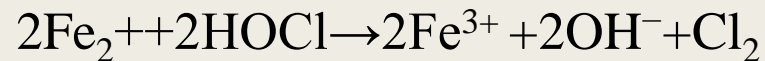


The  $Fe(OH)_3$  and  $Fe(OH)_2$  remains in the aqueous stream as a gelatinous suspension, which can remove the pollutants from wastewater either by complexation or by electrostatic attraction, followed by coagulation.

- Ferrous and ferric ions hydrolyze in water and form various monomeric and polymeric species whose proportions depend on the ferric ion concentration and on the pH:  $\text{Fe(OH)}^{2+}$ ,  $\text{Fe(OH)}_2^+$ ,  $\text{Fe(OH)}_2^{4+}$ ,  $\text{Fe(OH)}_4^-$ ,  $\text{Fe(H}_2\text{O)}_5(\text{OH})^{2+}$ ,  $\text{Fe(H}_2\text{O)}_4(\text{OH})_2^+$ ,  $\text{Fe(H}_2\text{O)}_8(\text{OH})_2^{4+}$ ,  $\text{Fe}_2(\text{H}_2\text{O)}_6(\text{OH})_4^{2+}$  and  $\text{Fe(OH)}_3$ .
- At lower pH values, chemical corrosion and pitting corrosion at both electrodes in the presence of some ionic compounds, such as chloride anions. At higher pH values, the dissolution efficiency decreases below the Faraday's law values because secondary reactions occur near the anode, including oxygen evolution. For alkaline pH, iron oxidation leads to Fe(III) formation through Eq. (20) as oxide or hydroxide species. This decreases the iron concentration produced, because Fe(III) formation requires 3 electrons instead of 2 for Fe(II) and so, a higher current value for achieving the same iron concentration is required. The various monomeric and polymeric species finally turn into amorphous  $\text{Fe(OH)}_3$  precipitates that are efficient for a rapid adsorption of soluble organic compounds and trapping of colloidal particles.
- Final pH usually achieved is 9 or 10 with Fe electrodes even when the initial pH is acidic

## An efficient operation of Fe-EC

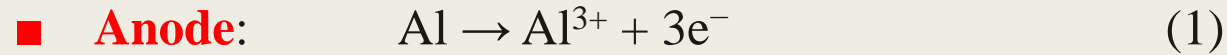
- $\text{Fe}^{2+}$  is highly soluble and therefore, not capable of an efficient colloid destabilization by  $\text{Fe}(\text{OH})_3$ , hereby causing poor EC performance. Consequently, an efficient operation of Fe-EC requires one or more of the following optimization techniques for the  $\text{Fe}^{3+}$  production
  - (a) aerating the water to increase the dissolved oxygen concentration and  $\text{Fe}^{2+}$  oxidation;
  - (b) increasing the pH to 7.5 or higher to promote the  $\text{Fe}^{2+}$  oxidation rate;
  - (c) introducing an alternative oxidant such as chlorine that may be produced by oxidization of the chloride ions present in water/wastewater on the iron anode or in an additional electrolysis cell, for example using a Ti/ $\text{RuO}_2$  anode and a Ti cathode. Thereafter, ferrous oxidation takes place in the bulk solution, as shown below:



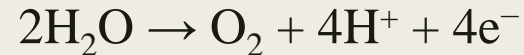
Taking into account the electric current consumed by chloride ions oxidation, this process is not efficient unless the water/wastewater to treat contains above 600 mg  $\text{Cl}^-/\text{L}$ .

- (d) increasing the residence time to achieve complete  $\text{Fe}^{2+}$  oxidation.

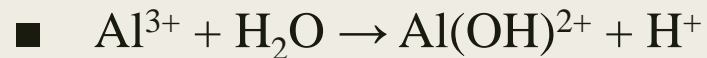
# Electrocoagulation with Aluminum Electrode



- When the anode potential is sufficiently high, secondary reactions may occur, especially oxygen evolution

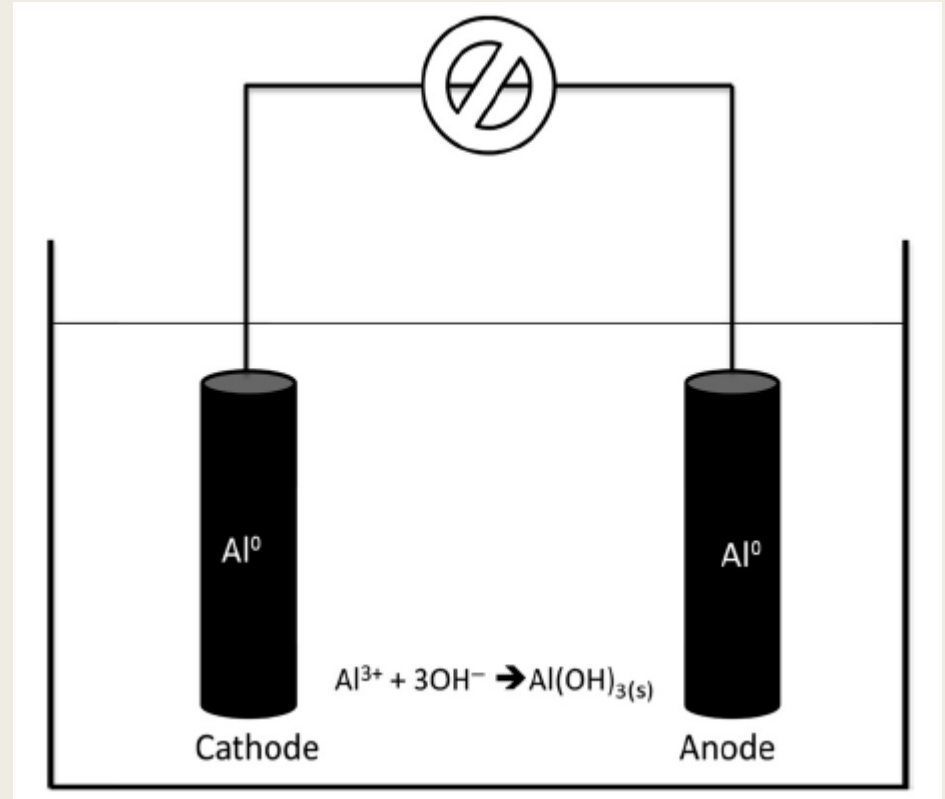
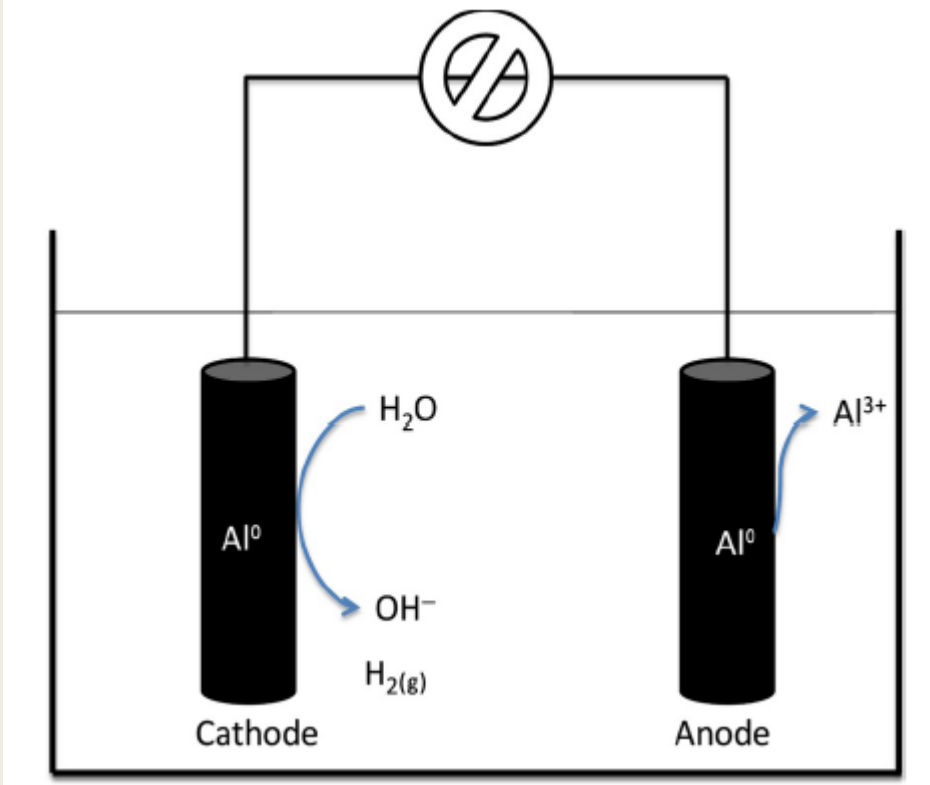


- Aluminum ions ( $\text{Al}^{3+}$ ) produced by electrolytic dissolution of the anode (Eq. (1)) immediately undergo spontaneous hydrolysis reactions which generate various monomeric species according to the following sequence (omitting co-ordinated water molecules for convenience):



- Actually, this is only an oversimplified scheme, since dimeric, trimeric and polynuclear hydrolysis products of Al can also form:  $\text{Al}_2(\text{OH})_2^{4+}$ ,  $\text{Al}_3(\text{OH})_4^{5+}$ ,  $\text{Al}_6(\text{OH})_{15}^{3+}$ ,  $\text{Al}_7(\text{OH})_{17}^{4+}$ ,  $\text{Al}_8(\text{OH})_{20}^{4+}$ ,  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ ,  $\text{Al}_{13}(\text{OH})_{34}^5$

- As a result, monomeric and polymeric species induce finally the formation of the amorphous  $\text{Al}(\text{OH})_3$  “**sweep flocs**” which have large surface areas beneficial for a rapid adsorption of soluble organic compounds and trapping of colloidal particles



# Faraday's Law

- The amount of metal dissolved by anodic oxidization can be calculated using Faraday's law. The mass of metal  $m$  is, therefore, a function of the electrolysis time  $t$  and of the electric current  $I$ :

- $$m = \phi \frac{It}{nF} M$$

- $M$  is the atomic weight of the electrode material

- $F$  is Faraday's constant. However, Faraday's law ( $\phi = 1$ ) is valid only when all the electrons in the system participate only in the metal-dissolution reaction at the anode. When parallel reactions occur, a correction factor, denoted *current efficiency or faradic yield* ( $\phi$ ), is used to account for the gap between the theoretical and experimental dissolution of the sacrificial anode. This value is usually lower than 1 but  $\phi$  may be higher than 1 when the chemical and the electrochemical oxidation mechanisms of the metal proceed simultaneously.

- The metal cations released in the bulk undergo various equilibrium reactions that correspond to acid/base, complexation, precipitation and redox reactions in water.

# Key parameters influencing the EC process

The parameters affecting EC effectiveness are related

- to the operating conditions such as current or voltage and operation time,
- to water/wastewater features such as pH, alkalinity and conductivity and
- to the geometry of the EC reactor and the EC electrodes (electrode surface, electrode spacing).



# Anode Material

- Traditionally, the electrodes used in electrocoagulation are Fe and Al. However, recent research indicate that Cu and Zn can be used.

# Ambient Temperature

- Increase on water temperature prevents the formation of sediments on the surface of electrodes and facilitates the rate of passivating film dissolution.
- Active aluminum anode dissolution occurs at water temperatures between 2 and 60C, and a current density of 1-4 mA/cm<sup>2</sup>. Higher temperature leads to decrease in the yield of aluminum and the current increases in the voltage across the electrodes. The maximum CE during steel electrode dissolution is achieved in a temperature range of 10-25C and an applied current density of about 6 mA/cm<sup>2</sup>.

# Effect of current

- Current  $I$  is a key parameter of EC. EC is often designed as a function of current density  $j$  defined as the ratio of current over electrode surface area  $A$ .
- $J=I/A$
- Current density determines the coagulant dosage at the anode and the hydrogen gas ( $H_2$ ) evolution at the cathode governed by Faraday's law. The bubble density affects the system hydrodynamics, which in turn influences mass transfer between pollutants, coagulant and gas micro-bubbles, and finally dictates collision rate of coagulated particles that results in flocs formation. In the case of the bubble generation, if the applied current is low the number of bubbles is small, so this favors the sedimentation of the flocs. With higher applied currents, the bubble generation increases. Thus, the combination of increased aggregation and bubble production makes flotation the primary removal mechanism.
- Current density affects as well hydrolyzed metal species through pH evolution during EC process as a function of water alkalinity.
- The current appears, therefore, to create a dynamic physical/chemical environment that governs directly the coagulation/flocculation mechanism and favors the electromigration of ions and charged colloids.
- However, very high current values may negatively affect the EC efficiency. For instance, secondary reactions may occur chiefly, and overdosing can reverse the charge of the colloids and redisperse them leading thereby to a decrease of the coagulant efficiency and to a reduction of the electrode lifetime.
- Optimum current density should be determined considering other operating parameters. To operate the EC system for a long period without maintenance, current density is suggested to be between 20 and  $25 \text{ A}\cdot\text{m}^{-2}$

## Energy consumption

- Cell voltage is correlated as a function of equilibrium potential, anode and cathode overpotential. Electric energy consumption can then be deduced as a function of operation time  $t$  using:
- $P = \int_0^t U I dt$
- As electric energy required for the EC process is linked to the electric current and potential. EC can be driven either under the galvanostatic or potentiostatic mode. For the **galvanostatic** mode, EC process is carried out by controlling and/or varying the current applied through electrodes while for the **potentiostatic** mode, it is the applied cell voltage that is controlled and/or varied as a function of amount of coagulant desired to be released in EC reactor. The **potentiostatic** mode is **rarely used for EC** and often used for other electrochemical methods such as electro-oxidation and electro-reduction when sacrificial electrodes are not used

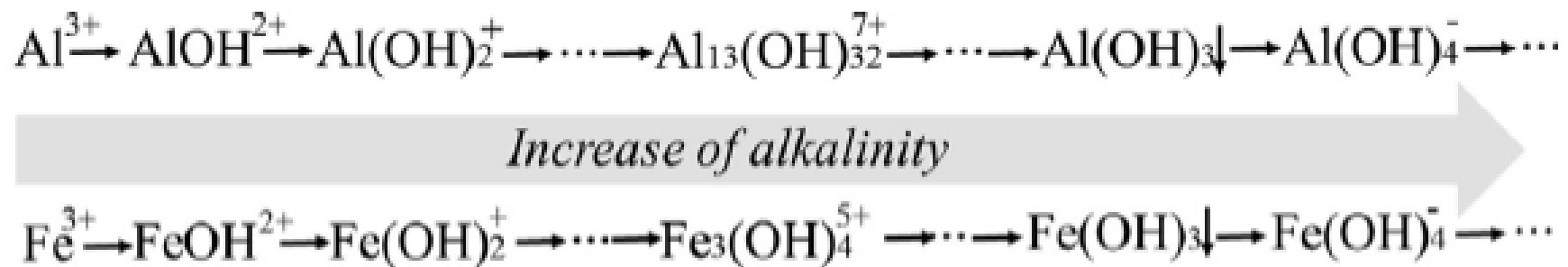
High current also increases voltage and ohmic drop between anode and cathode; ohmic drop or IR drop results from the ohmic resistance of the electrolyte  $R$ , which can be expressed as follows:

$$R = \frac{d}{A} \frac{1}{k}$$

where  $d$  denotes the inter-electrode distance and  $k$  the water conductivity. Indeed, when  $i$  increases, and  $U$  tends to the IR drop term  $RI$  deduced from above Eq. , which means that electric power varies as  $RI^2$ . Consequently, power input can be reduced by decreasing the distance between the electrodes and increasing the electrode surface area and the water/wastewater conductivity. Using current reversal (switching anode and cathode electrically) is useful to reduce maintenance cost, but its effect on pollution removal is not ascertained up to now.

# Effect of water pH and alkalinity

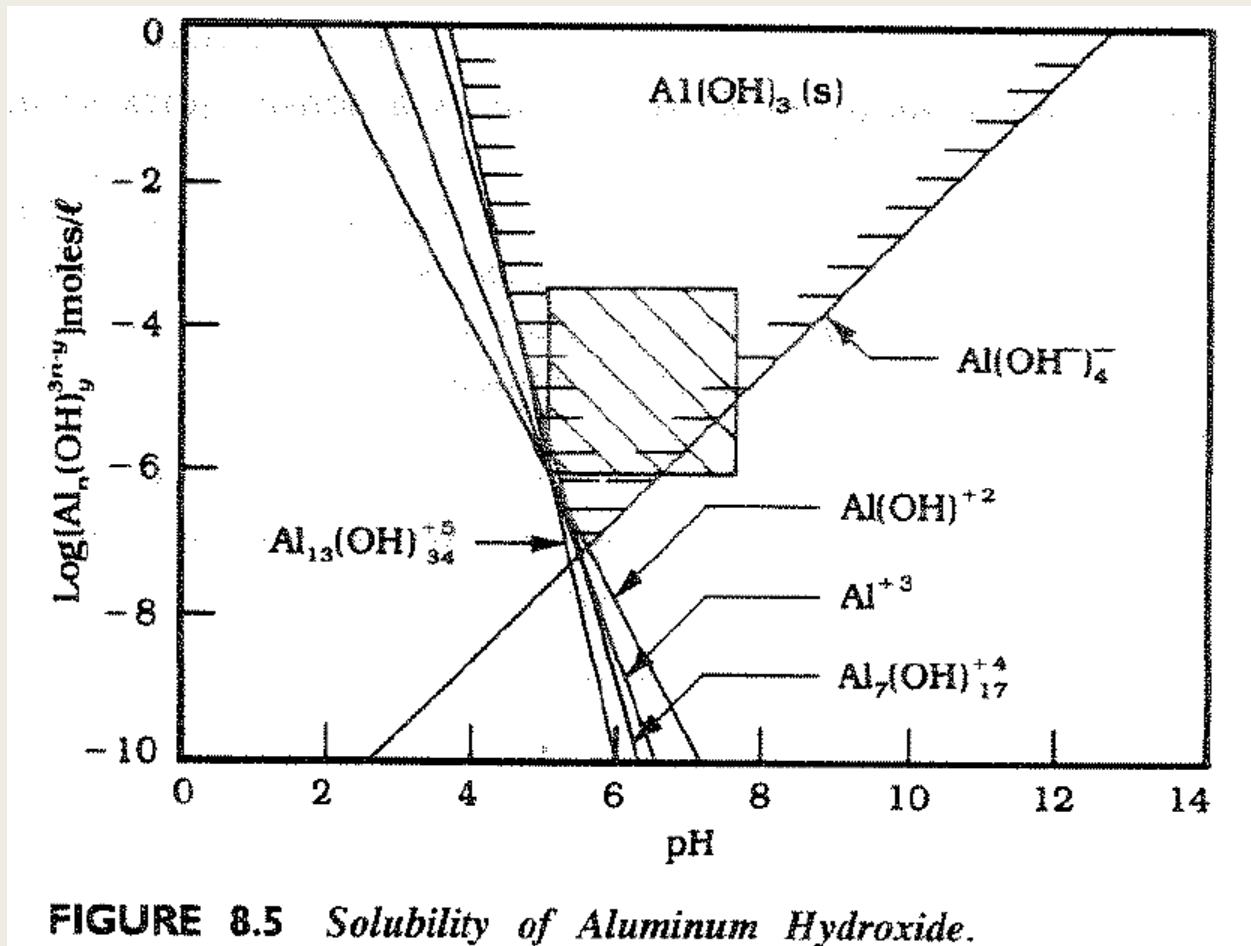
- pH is another key factor influencing the performance of EC, especially the coagulation mechanism because it governs the hydrolyzed metal species generated in reactive media and influences the prevailing mechanisms of EC
- Precipitation of  $\text{Al}(\text{OH})_3$  and  $\text{Fe}(\text{OH})_3$  occurs in the range of neutral pH and also contributes to the removal of pollutants from water initiating sweep flocculation process. Growing in size positively charged  $\text{Al}(\text{OH})_3$ /  $\text{Fe}(\text{OH})_3$  aggregates electrostatically attract the negatively charged pollutants, which results to pollutants neutralization and destabilization thus precipitating them. Nevertheless, the positive effect of counterions on colloids destabilization, the dosage of coagulant should be carefully controlled to avoid the charge reversal and restabilization of colloids.



Dependence of aluminum and iron polynuclear hydroxo complexes formation on pH.

- **pH-Al**

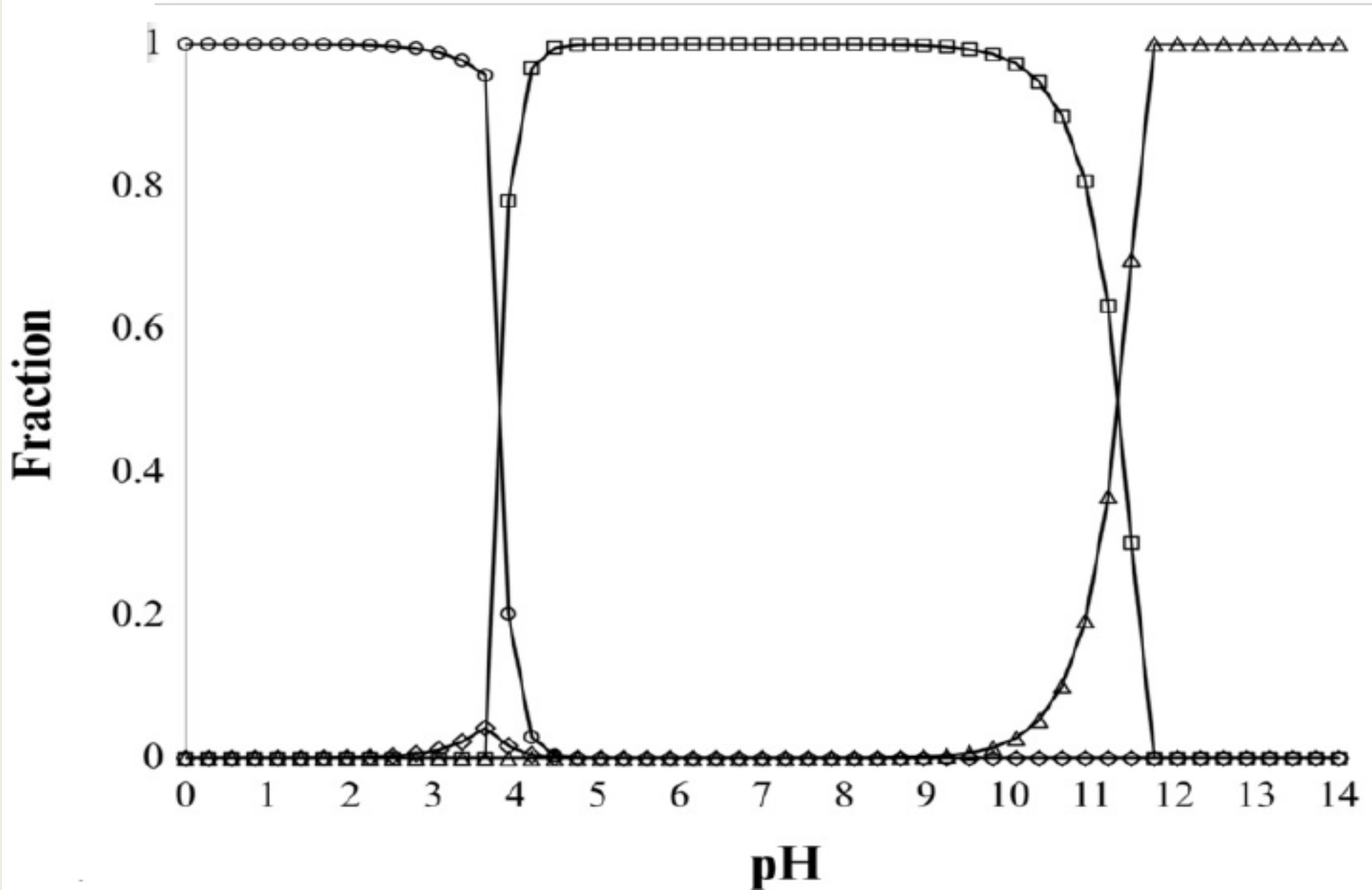
- In practice, soluble  $\text{Al}^{3+}$  cations prevail when pH is lower than 4, soluble aluminate anions prevail when pH is higher than 10, while the insoluble  $\text{Al}(\text{OH})_3$  form predominates otherwise. The formation of polymeric species has also been reported:  $\text{Al}(\text{OH})_{15}^{3+}$ ,  $\text{Al}_7(\text{OH})_{17}^{4+}$ ,  $\text{Al}_8(\text{OH})_{20}^{4+}$  and  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ . The Lewis acidity of aluminum counterbalances the formation of  $\text{OH}^-$  anions at the cathode, which induces a buffer effect and leads to a final pH between 7 and 8 which strongly differs from conventional chemical coagulation using Al salts. As a result, monomeric and polymeric species induce finally the formation of the amorphous  $\text{Al}(\text{OH})_3$  “sweep flocs” which have large surface areas beneficial for a rapid adsorption of soluble organic compounds and trapping of colloidal particles
- While conducting electrolysis process with aluminum anodes, a significant change of pH values is observed after the treatment process. Increase of pH is observed in acidic media (pH up to 4) and decrease of pH occurs in the case of alkaline solutions (pH above 8-9). In the case of neutral solutions insignificant shift of pH to more positive values can be observed. This is explained by buffering capacity at these pH and production of hydroxyl ions at cathode. The decrease of pH in alkaline conditions ions can be explained by the formation of  $\text{AlOH}_4^-$  complexes. Acidic (pH < 4) and alkaline (pH > 8) conditions lead also to the enhanced aluminum anode dissolution. This is explained by the solubility of the oxide films at these conditions and as a consequence elimination of passivation film, which prevents electrochemical and chemical metal dissolution. While using iron anodes for electrocoagulation, significant increase of pH is observed analogous to aluminum anodes .



**FIGURE 8.5** *Solubility of Aluminum Hydroxide.*

**FIGURE 8.5** *Solubility of Aluminum Hydroxide. (Shaded area is the usual operating region used in water treatment.)*

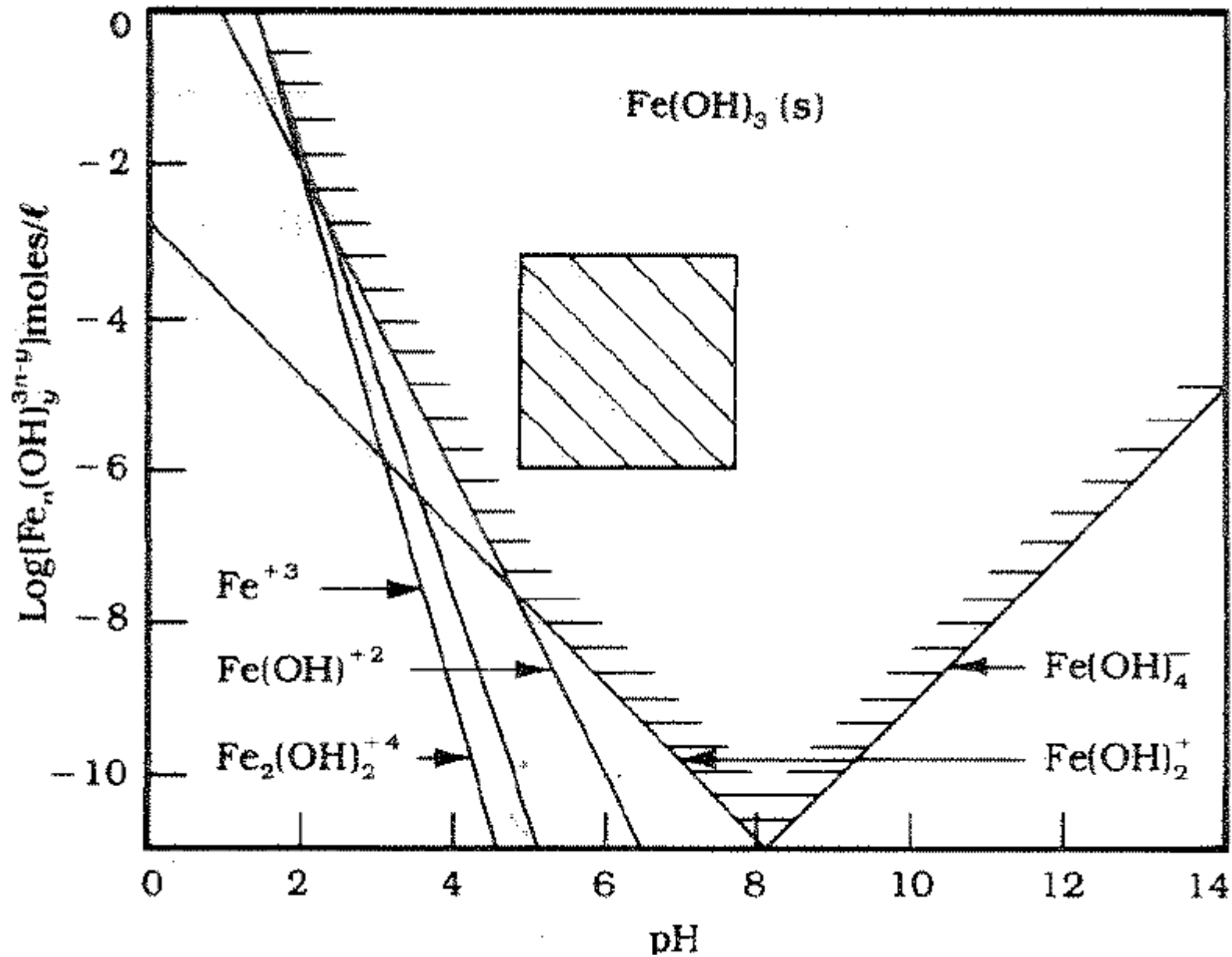




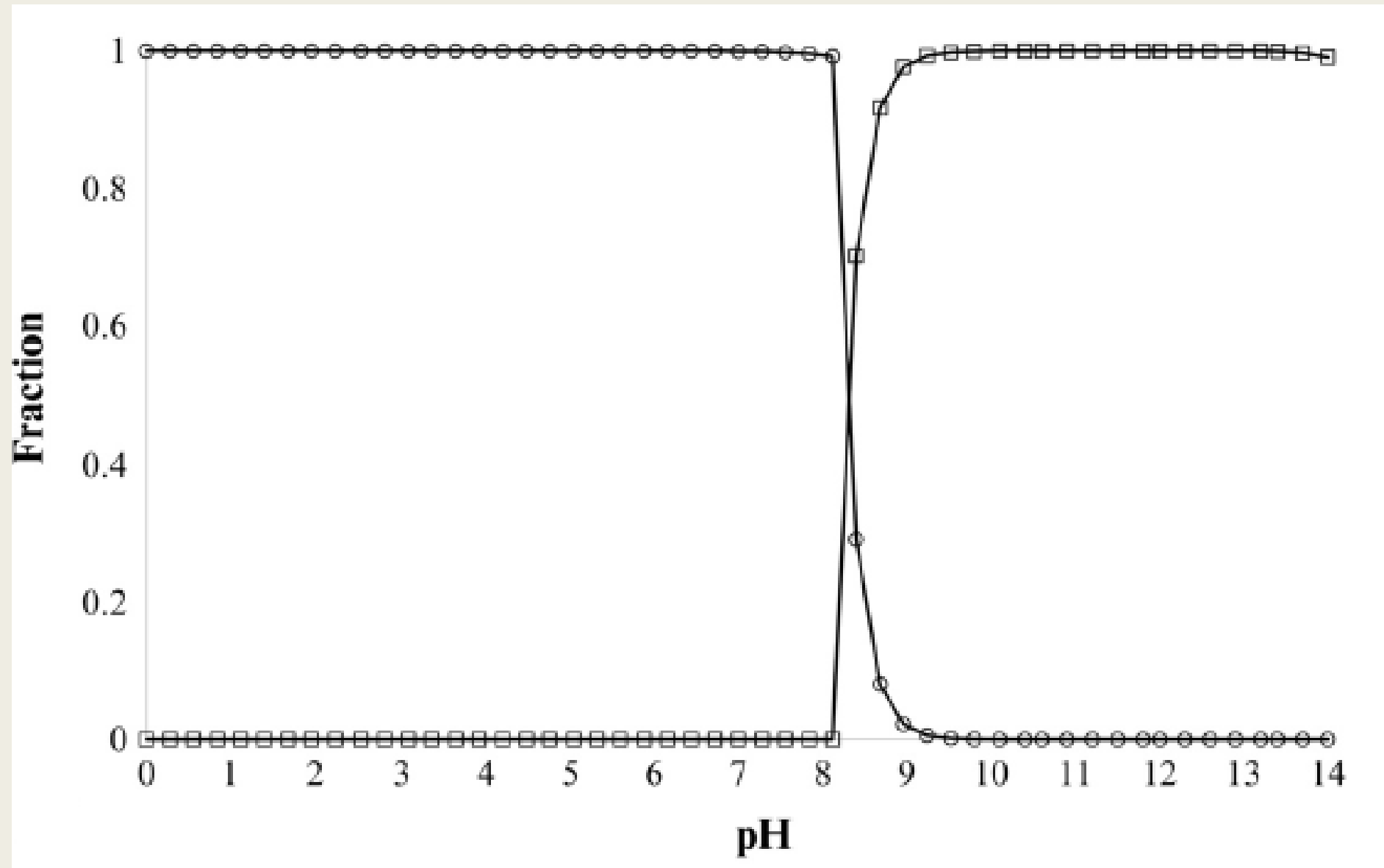
Chemical species diagram of Al [ $\text{O}$   $\text{Al}^{3+}$ ;  $\square$   $\text{Al}(\text{OH})_3(\text{cr})$ ;  $\triangle$   $\text{Al}(\text{OH})_4^-$ ;  $\diamond$   $\text{Al}(\text{OH})^{2+}$ ] species in an aqueous solution.

- pH -Fe

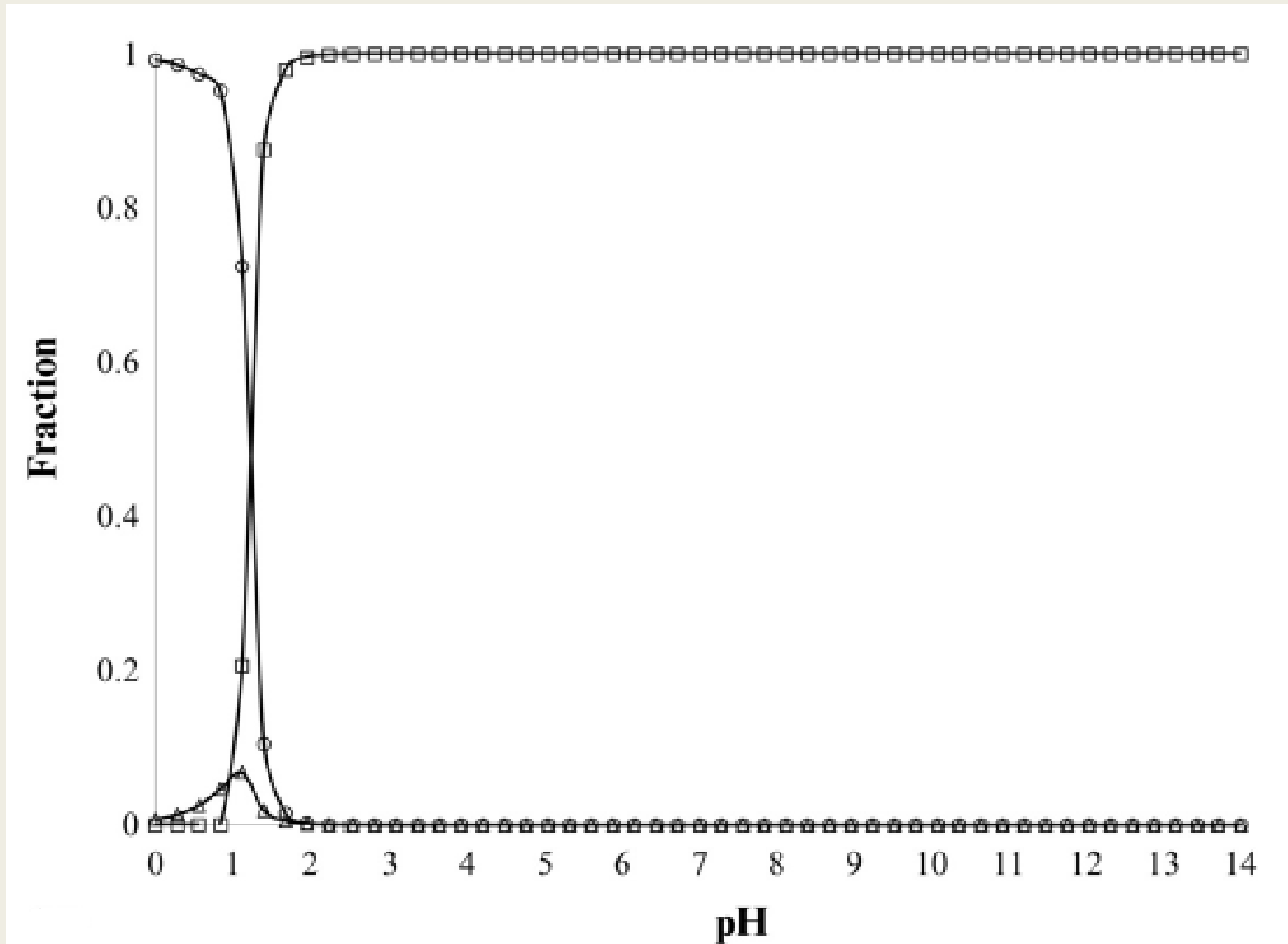
- For Fe electrode, the quantity of insoluble iron hydroxide drastically increases with pH ranging from 4 to 7. At this latter pH value, iron hydroxide ions are absent on the predominance diagram.
- In acidic conditions the cation is readily available for a reaction, and when the pH is raised hydroxocomplexes start to appear. This implies that solution reactions will have different reaction rates and the process efficacy will be reduced. At low pH values, the simple cation form of the metal is present. However, once the pH is increased the hydro-complexes of the cations start to appear. In the case of iron, Fe(II) has a larger pH window in which it can be a free cation; on the other hand, Fe(III) has a small range of pH values in which it can be present as the cation. This implies that redox reactions in an aqueous solution could affect the effectiveness of the pollutant removal process.
- Effluent pH after EC treatment would increase for acidic influent but can decrease for alkaline effluent, which is due to the buffering effect of EC. The increase of pH in acidic medium is due to hydrogen evolution at the cathode while the decrease of pH is due firstly to the formation of hydroxide precipitates that release  $H^+$  cations at the anode vicinity and the secondary reactions such as water oxidation and chlorine production and its hydrolysis. This highlights the buffering effect of EC that acts in addition to that of water alkalinity. This effect is particularly high with Al electrodes because of the formation of aluminate anions at high pH.
- The bicarbonate alkalinity has been reported to improve slightly the pollutants removal efficiency and in addition it allows to remove the hardness by precipitation of  $CaCO_3$  thanks to the hydroxyl anions produced by water reduction at the cathode vicinity.



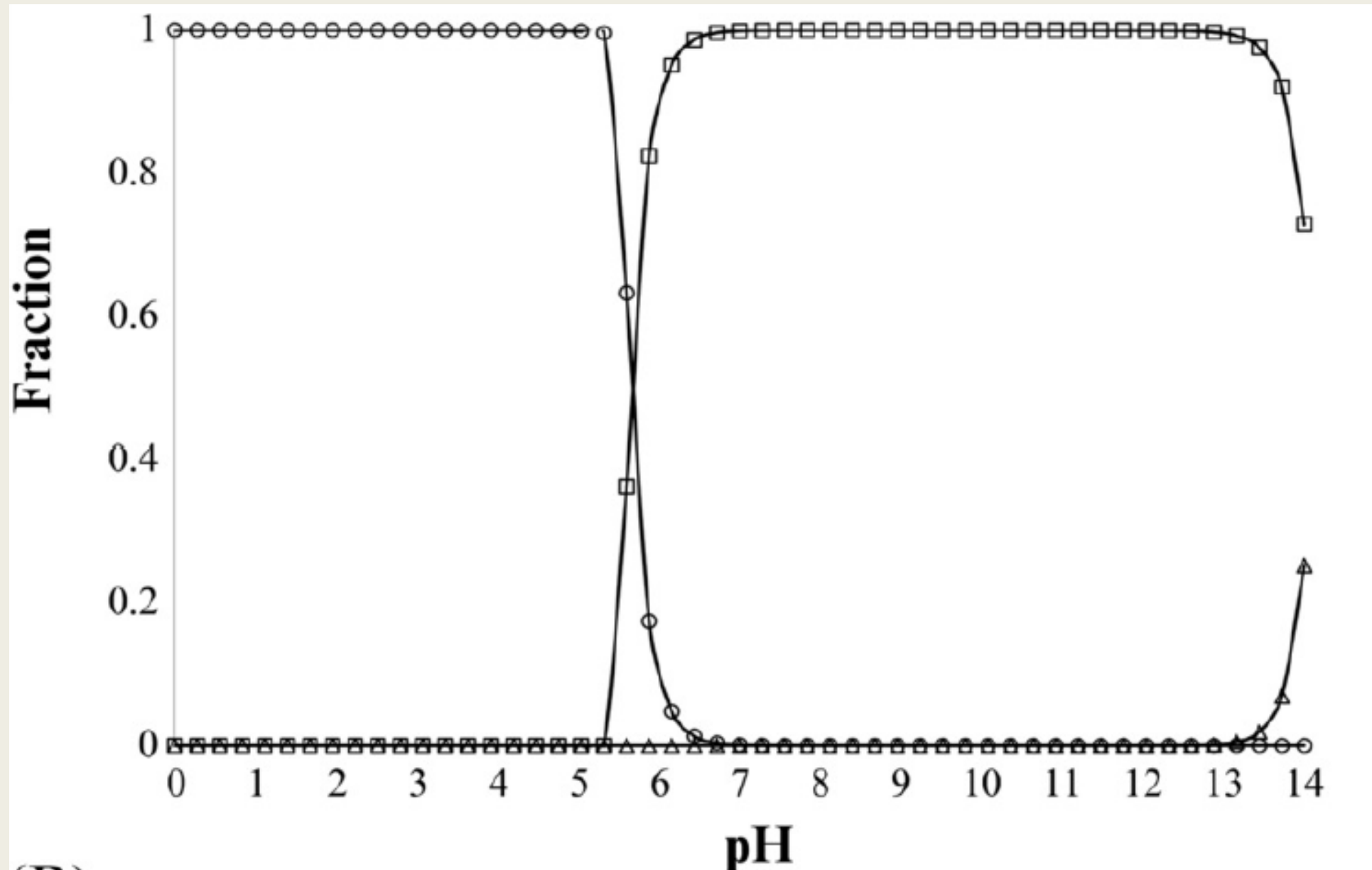
**FIGURE 8.6** Solubility of Ferric Hydroxide. (Shaded area is the usual operating region used in water treatment.)



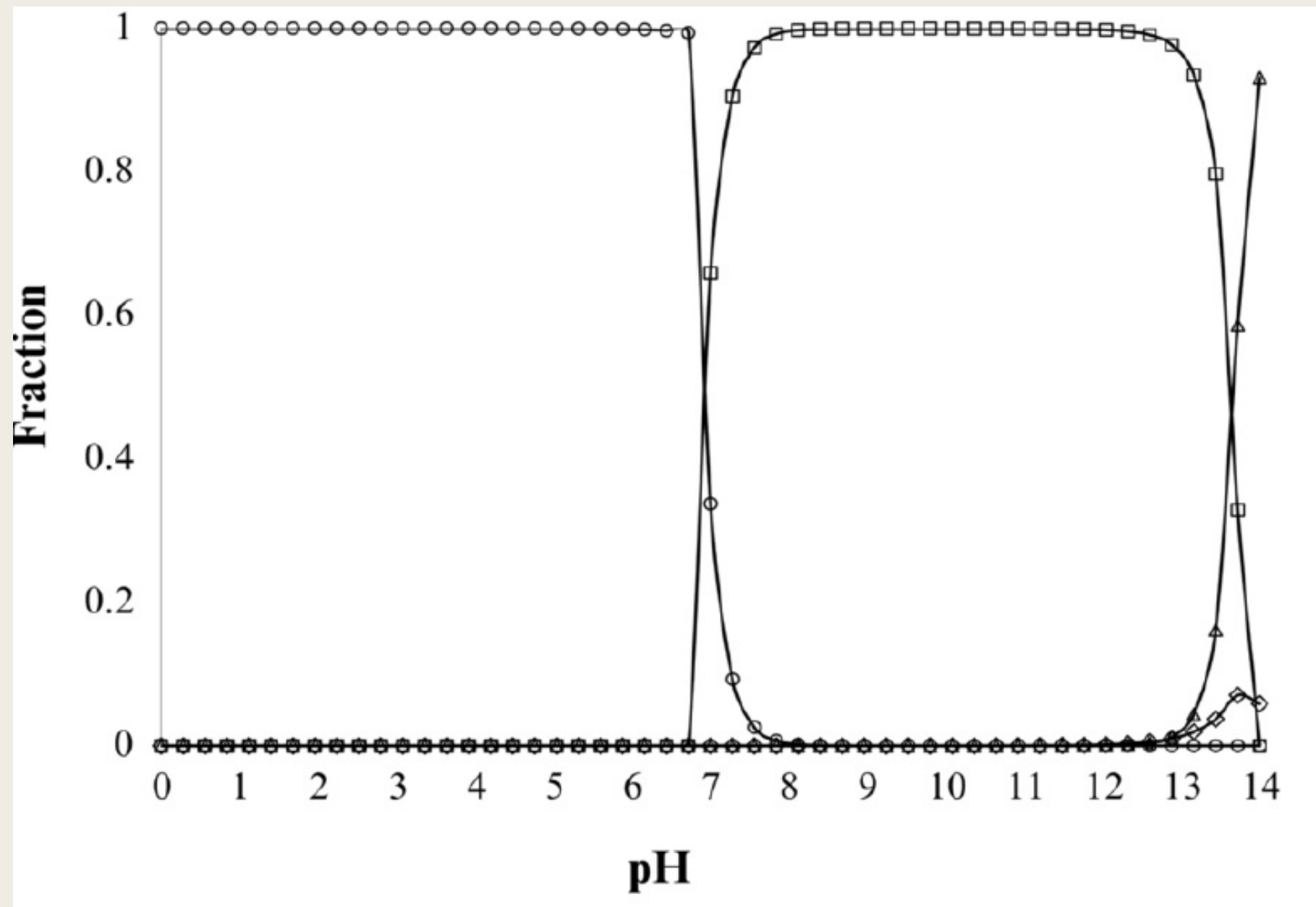
Chemical species distribution diagrams of Fe(II) [○: Fe<sup>2+</sup>, ◻ : Fe(OH)<sub>2(s)</sub>] species in an aqueous solution.



Chemical species distribution diagrams of Fe(III) [○: Fe<sup>3+</sup>; ◻: Fe<sub>2</sub>O<sub>3</sub>(cr); ◄: Fe(OH)<sup>2+</sup>] species in an aqueous solution.



Chemical species diagram of Cu(II) [○  $\text{Cu}^{2+}$ ; □  $\text{Cu}(\text{OH})_4^{2-}$ ; △  $\text{CuO}(\text{cr})$ ] species in an aqueous solution.



Chemical species diagram of Zn(II) [○  $\text{Zn}^{2+}$ ; □  $\text{ZnO}(\text{cr})$ ; △  $\text{Zn}(\text{OH})_4^{2-}$ ; ◇  $\text{Zn}(\text{OH})_3^-$ ] species in an aqueous solution.

# Electrodes arrangement

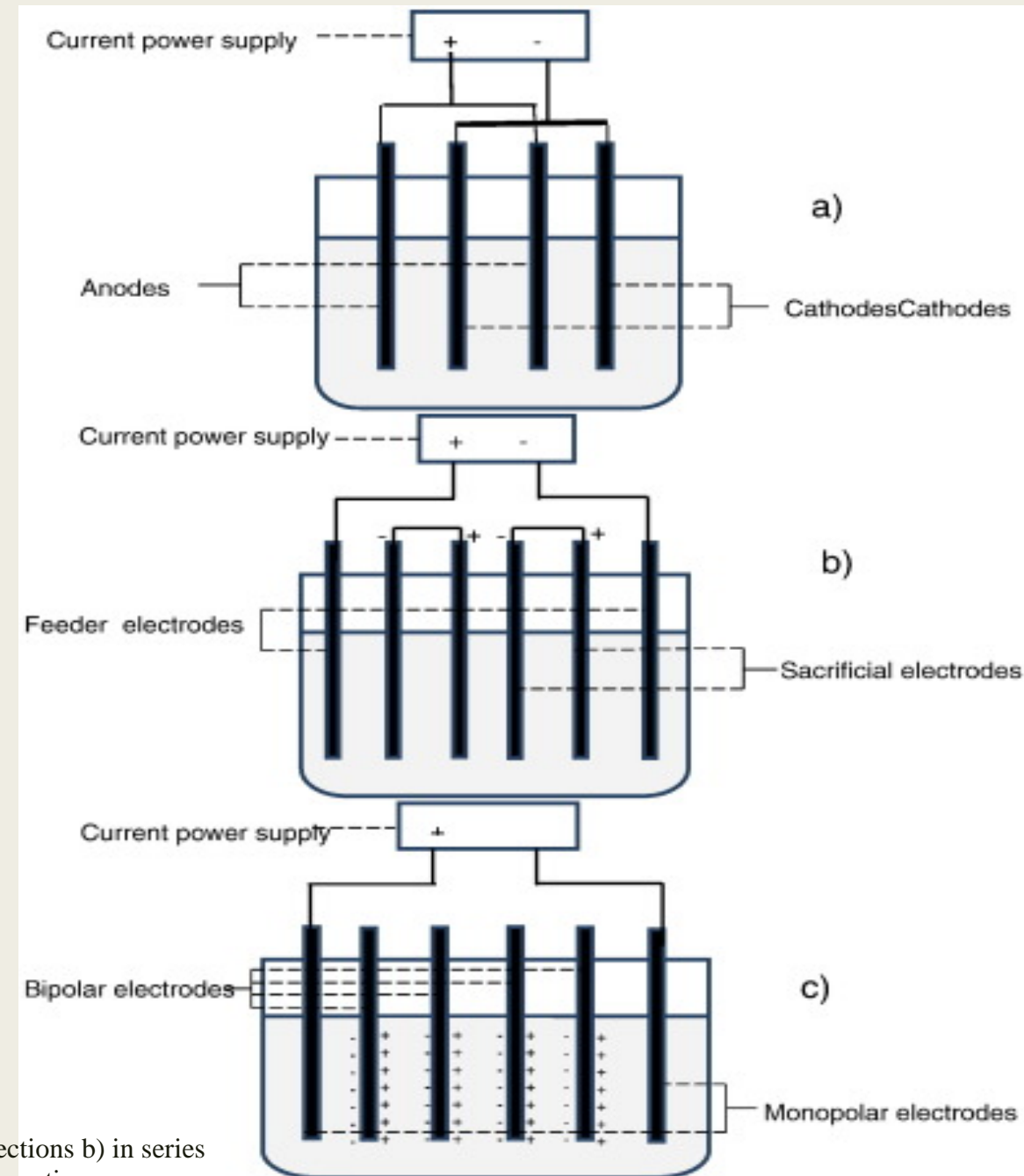
- EC process can be affected by electrode system through electrodes arrangement and inter-electrode distance. Electrodes arrangement can either be simply composed of an anode and a cathode or be composed of many anodes and cathodes complexly settled in EC cell. The complex electrodes arrangement can be classified in monopolar and bipolar electrodes.



- Monopolar electrodes in parallel connection (MP-P) are described in Fig.a. It corresponds to an electrode arrangement that consists of cathodes and anodes placed alternatively at the same anodic or cathodic potential, respectively. Each pair of cathode/anode corresponds to a small electrolytic cell in which the voltage is the same. The reactor consists, therefore, of electrolytic cells in parallel. Consequently, the current of each electrolytic cell is additive.

- Monopolar electrodes in series connections (MP-S) are described in Fig.b. Each pair of internal sacrificial electrodes is internally connected with each other, and has no interconnections with the two outer electrodes. In this case, the electric current passing through all the electrodes is the same, whereas the global voltage is the sum of voltage in each individual electrolytic cell.

- Bipolar electrode in series connections (BP-S) comprises two outer electrodes connected to electric power supply and the sacrificial electrodes placed between the two outer electrodes (Fig.c). Outer electrodes are monopolar and the inner ones are bipolar. The bipolar electrodes are not interconnected and each of their sides acts simultaneously as an anode and a cathode. This means that opposite sides of each bipolar electrode are oppositely charged, the anodic dissolution takes place on the positive side while the negative side is prone to cathodic reactions.



■ Fig.. Monopolar electrode a) in parallel connections b) in series connections; c) bipolar electrode in series connections.

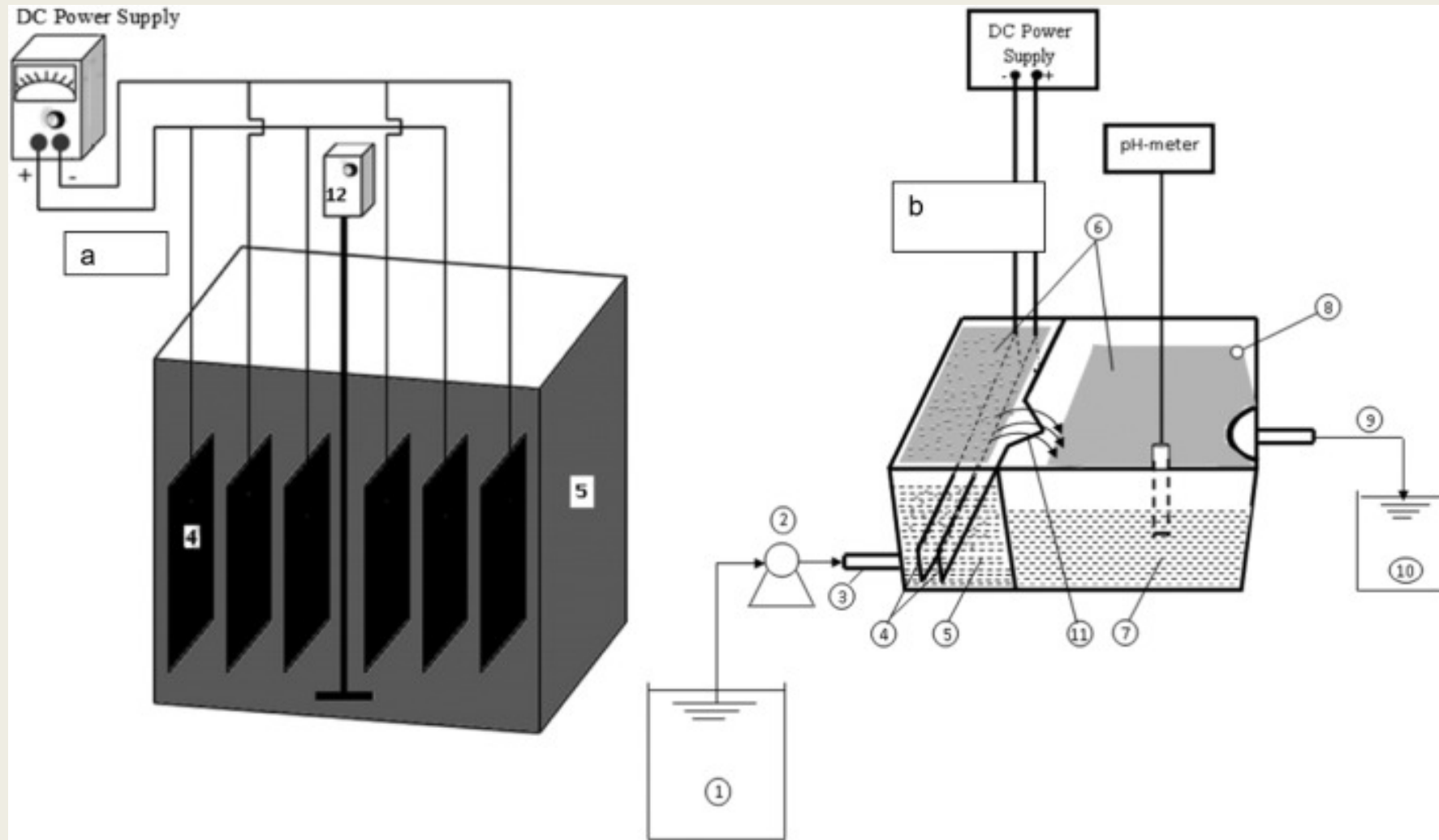
- Overall, monopolar electrodes require a low voltage and a higher current contrary to the bipolar electrodes that operate under a high voltage and a lower current. It is so difficult to conclude which electrodes arrangement is better than the other considering only EC yield given that it has been proved that equally BP-S could display a high EC efficiency. Taking into account the ratio effectiveness-cost, monopolar electrodes may be deemed interesting because in many cases this electrodes arrangement offers a high pollutant removal with a lower energy consumption, knowing that bipolar electrode always consumes a high energy . This last mode which is easy to handle, needs less maintenance cost during operation, thus the impact of maintenance cost on overall operation cost should equally be considered to choose an appropriate electrode mode.
- Besides the popular rectangular electrodes, there are other geometrical shapes such as circular, cylindrical. Electrodes can be settled either vertically or horizontally in EC cell. Despite being rarely used, horizontal electrodes in EC batch reactor may have a higher mixing efficiency

# Distance and Water Flow Rate Between Electrodes

- To reduce the EC during the electrolysis process, the distance between electrodes should be reduced, because the greater the distance between electrodes, the higher the EC. In this regard the optimal distance between electrodes is in the range of 10-20 mm. The higher the water flow rate between electrodes, the faster the anodic metal dissolution, which prevents the metal oxide films formation. Consequently, the higher the water flow rate, the lower the EC and passivation of electrodes.
- The IR-drop increases as the distance between electrodes increases. Thus, energy consumption decreases with decreasing the gap between electrodes. As the distance between electrodes becomes lower, more electrochemically generated gas bubbles bring about turbulent hydrodynamics, thereby leading to a high mass transfer as well as to a high reaction rate between the coagulant species and pollutants. In addition, inter-electrode gap defines the residence time between the anode and the cathode for a continuous system and the time of treatment for a batch reactor for reaching a desirable EC efficiency. For a complex electrode arrangement, Inter-electrode distance determines also the number of electrodes to place in electrocoagulation cell, once its volume is defined.

# EC reactor design

- EC reactor design is of great importance since it affects the overall performances of the EC process through its influence on the operating parameters namely, flow regime, flocs formation, removal yield and flotation/settling characteristics. EC reactors have been designed following some key criteria, chiefly the operating mode and the goals to be reached. EC reactor design can be classified on the basis of three major distinctions according to literature survey.
- The first one is whether a reactor is configured as a batch or a continuous system, i.e. the feed mode. For a continuous system, reactors are continuously fed in water/wastewater and operate, while the operation is carried out with a fixed wastewater volume per treatment cycle in a batch process.
- The second distinction is the method used to separate the aggregated pollutants.
- The last one is the design of the electrodes geometry that defines the current distribution in the cell. In practice, rectangular cells still dominate, as planar rectangular electrodes can be used, and the most common design in typical applications is the open vertical-plate cell, usually followed by a settler (Fig.). This means that it is open at the top, which avoids submerged contacts and make maintenance easier; vertical anodes and cathodes are equally spaced in parallel; any vertical/horizontal length ratio can be used, which makes scale-up easy, but maintenance is facilitated by values lower than 2. If current reversal is applied, the symmetry of the anode-cathode electrodes reduces maintenance, in particular in comparison to cylindrical EC cells. Described as the most versatile design in terms of flow rate, mixing is usually the main weakness of this cell geometry (Fig. b).



- Fig. Experimental setup of a) batch EC cell b) continuous EC cell (1: wastewater tank; 2: peristaltic pump; 3: effluent input to the first compartment; 4: electrodes; 4: EC cell /first compartment treatment; 6: sludge; 7: second compartment treatment; 8: sludge evacuation; 9: treated effluent evacuation; 10: treated water tank; 11: outfall; 12: mechanical stirrer).

- Alongside electrodes arrangement and electrodes spacing, EC reactor design affects EC through the reactor working volume that intervenes to define electrode area/volume ratio ( $A/V$ ) and through EC geometry. Electrode  $A/V$  ratio is the only key scale-up parameter in plant design that allows developing EC full-scale equipment from laboratory experiments keeping the same inter-electrode distance when using electrode plates. The typical range of electrode  $A/V$  ratio varies between  $15 \text{ m}^2/\text{m}^3$  and  $45 \text{ m}^2/\text{m}^3$ . An increase of the  $A/V$  ratio results in a decrease of both treatment time and the optimum current density .
- When the electrode area is high enough, the major parameter is the current concentration  $I/V$ . This parameter combines the current density and the electrode area/volume ratio and allows defining the concentration of coagulants released in water at a given treatment time under batch conditions. Under continuous system, the reactor volume allows defining the residence time for a considered flow rate of water/wastewater and thus the released coagulant quantity can be deduced.
- $C=(M/ZF)(1/V \cdot)t$
- where  $C$  and  $V$  are the theoretical concentration of metallic cations ( $\text{g}/\text{m}^3$ ) and the working volume of the EC device ( $\text{m}^3$ ), respectively.

# Effect of water conductivity

- The current density efficiency depends strongly on conductivity and ionic strength of water/wastewater.
- The current density efficiency increases with increasing electrolytic conductivity due to the decrease of ohmic resistance of water/wastewater.
- Conductivity also decreases the treatment time required to reach a given removal yield . Consequently, the energy consumption (UI) is reduced.
- NaCl is frequently used to increase the electrolytic conductivity. Chloride anions take part as well in the reduction of the adverse effects of other anions to avoid the precipitation of calcium carbonate in hard water that could form an insulating layer on the surface of the electrodes. For very high current density, chloride anions can also be oxidized to active chlorine forms, such as hypochlorite anions, that can oxidize organic compounds and ferrous ions or contribute to water/wastewater disinfection. In order to ensure a normal operation of EC in wastewater treatment, it is recommended that 20% of the anions present should be  $\text{Cl}^-$ .
- However, there are the constraints imposed on conductivity increase in wastewater treatment and particularly in potable water treatment. For wastewater treatment, besides a secondary pollution that could be produced by an increase of conductivity, there are the norms to be respected depending on whether the treated wastewater is devoted either to the reuse or to be flowed out in ecosystem. Conductivity increase during the treatment of drinking water by EC is highly limited in accordance with the standard norms that define the maximum chloride concentration in industrial effluents at 250 mg/L.

# Anionic Composition of Electrolyte

- The presence of anions in the water has a significant impact on the corrosion and consequently dissolution of the anode. Among different anions chloride ions have the greatest impact on the aluminum anode activity because of their small dimensions and ease of penetration through the oxide film. A subsequent oxygen displacement by chloride results in the inhibition of oxide film formation and enhanced Al corrosion. Chloride ions cause 1000 times more severe corrosion than the equivalent amount of sulfates. The effect of different anions on the enhancement of Al corrosion reduces in the following order:
  - $\text{Cl}^- > \text{Br}^- > \text{J}^- > \text{F}^- > \text{SO}_4^{2-} > \text{NO}_3^- > \text{PO}_4^{3-}$



# Anode passivation

- Formation of oxide films on the electrode surface (anode passivation) significantly hinders electrocoagulation.
- To prevent the sediments deposition on the electrodes, i.e., to prevent the passivation of electrodes, it is recommended to reverse the electrode's polarity with a periodicity of minutes, hours, or weeks.
- The higher the current density, the more often polarity of electrodes should be changed.
- Despite the positive effect of polarity reversal, it is not always effective for the removal of deposits because the CE drops significantly at the moment of polarity change.

# References

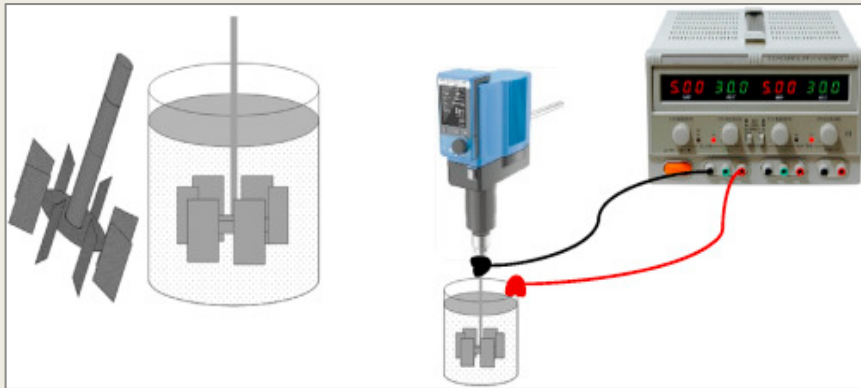
- G.Mouedhen, M.Feki, M. De Petris Wery, H.F.Ayedi, Behavior of aluminum electrodes in electrocoagulation process, *Journal of Hazardous Materials*, Vol.150, Issue 1, 2008, 124-135
- Jean Nepo Hakizimana, Bouchaib Gourich, Mohammed Chafi, Youssef Stiriba, Christophe Vial, Patrick Drogui, Jamal Naja, Electrocoagulation process in water treatment: A review of electrocoagulation modeling approaches, *Desalination* Volume 404, 17 February 2017, Pages 1-21
- Carlos Alberto Martínez-Huitle, Manuel A Rodrigo, Onofrio Scialdone (Eds), Electrochemical Water and Wastewater Treatment, 1st Edition, Elsevier, 2018
- Mika Sillanpää, Marina Shestakova, Electrochemical Water Treatment Methods, 1st Ed., Elsevier, 2017
- Christos Comninellis, Guohua Chen (Eds), Electrochemistry for the Environment, Springer, 2010

# Some of our Electrocoagulation Studies

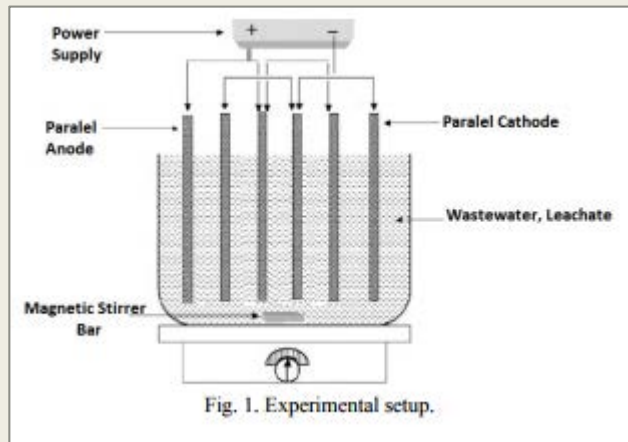
We applied the EC for wastewater treatment of different activities:

Wastewater Type	Initial Con. of Pollutant	Mode of the Process	Obtained Removal Efficiency	Remarks
chromium containing Electroplating wastewater	initial Cr(VI) concentration of 1000 mg/L	batch	~100%	produce value added ceramic pigments
tissue paper wastewater	COD: 1,220 mg/L	batch	92.6%	the sludge is evaluated as a catalyst in a fast pyrolysis process
cheese whey wastewater	COD: 15.500 mg/L	Continuous	86.4%	
Cattle Abattoir Wastewater	COD: 840 mg/L.	plug flow	90%	
yogurt industry wastewater	COD: 6500 mg/L	batch	84%	used as an iron source to produce brown and black inorganic ceramic pigments
Fluoride removal from water and wastewater	initial value of 5.0–0.12 mg/L	batch	97.6%	WHO-recommended fluoride limit of 1.2 mg/L at 0.5 mA/cm <sup>2</sup> was 5 min,
textile wastewater	COD: 1953 mg/L	a packed bed reactor, Continuous	96.88%	direct dischargeable effluent, complying with legal requirements, was obtained
cattle-slaughterhouse wastewater	COD: concentration (4200 mg L <sup>-1</sup> )	Batch	94.4%	
vegetable oil refinery wastewater	COD: 15,000 mg L <sup>-1</sup>	Batch	98.9%	its quality exceeded the direct discharge standard.
olive mill wastewaters	COD: 45,000 mg L <sup>-1</sup>	Batch	86%	

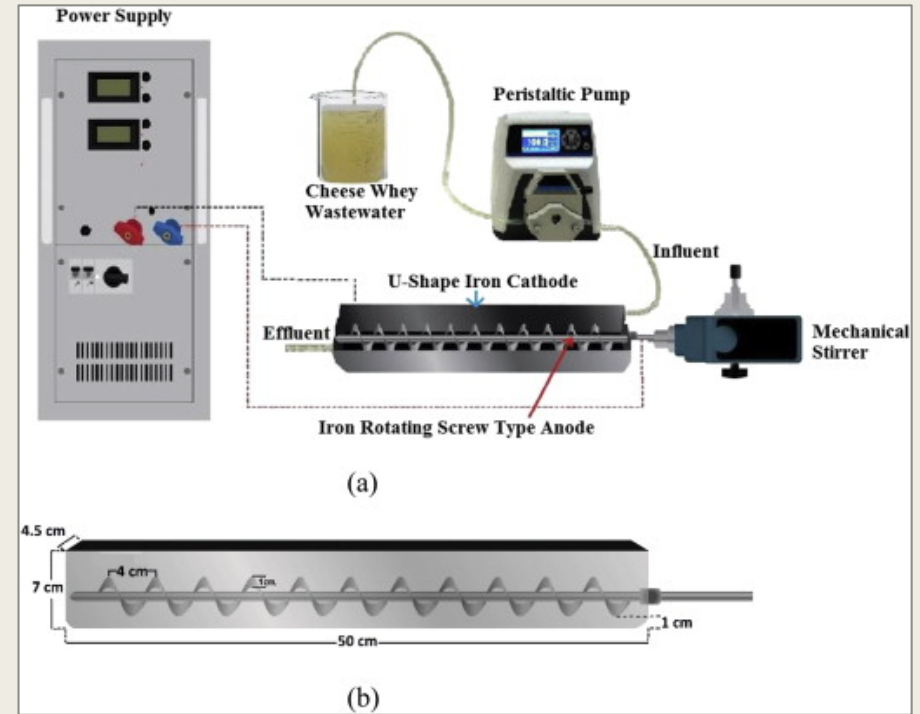
## Variety of Design and Configurations in Our EC studies



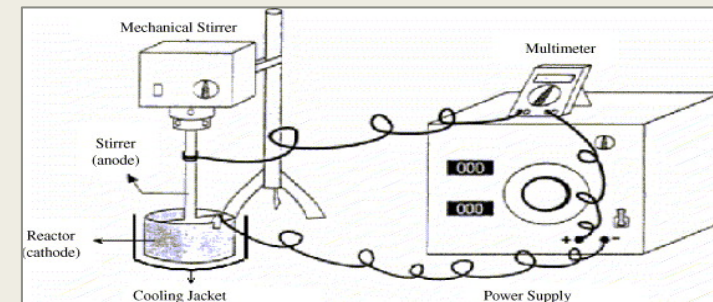
The treatment of chromium containing wastewater



Electrocoagulation of Landfill Leachate



Continuous electrocoagulation of cheese whey wastewater



Treatment of Vegetable Oil Refinery Wastewater

## Variety of Design and Configurations in Our EC studies

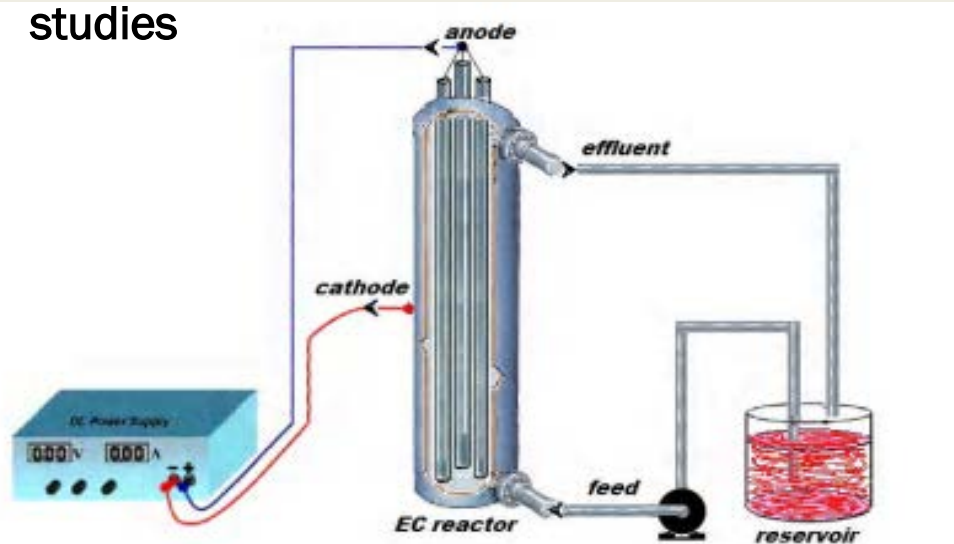
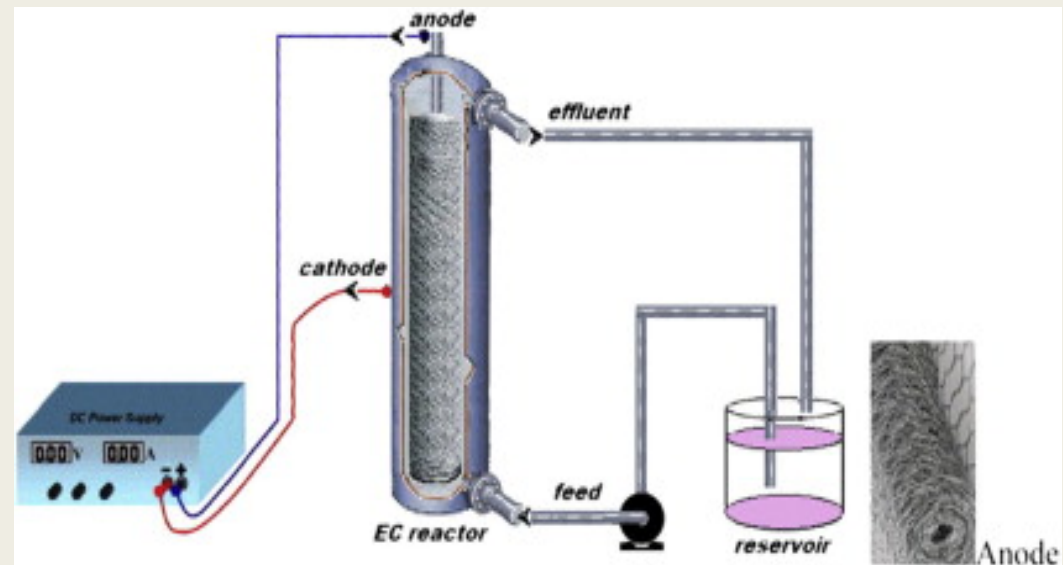
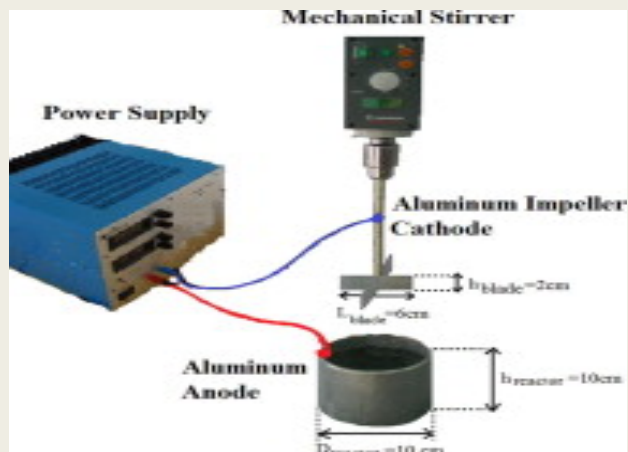


Fig. 1. Experimental setup

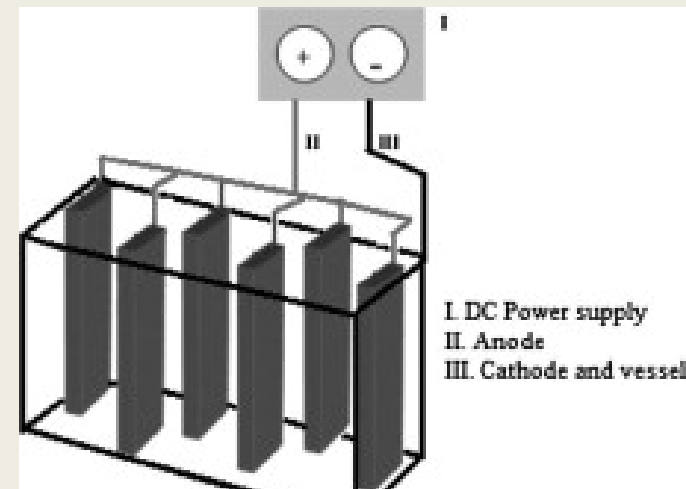


Treatment of Color and COD from Real Textile Wastewater with Packed Bed Reactor

## Treatment of Cattle Abattoir Wastewater in a Plug flow Reactor

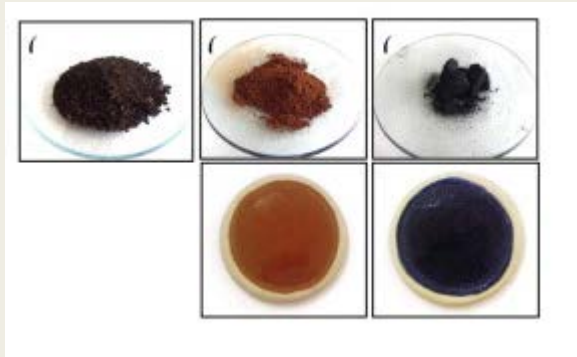


Fluoride Removal from Water and Wastewater with a Bach Cylindrical Electrode Using Electrocoagulation

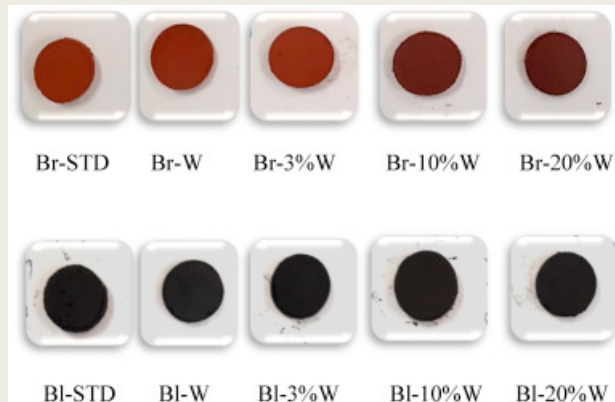


Yogurt Industry Wastewater and the Production of Ceramic Pigments from the Sludge

## Characterization and Use of Sludge for other applications



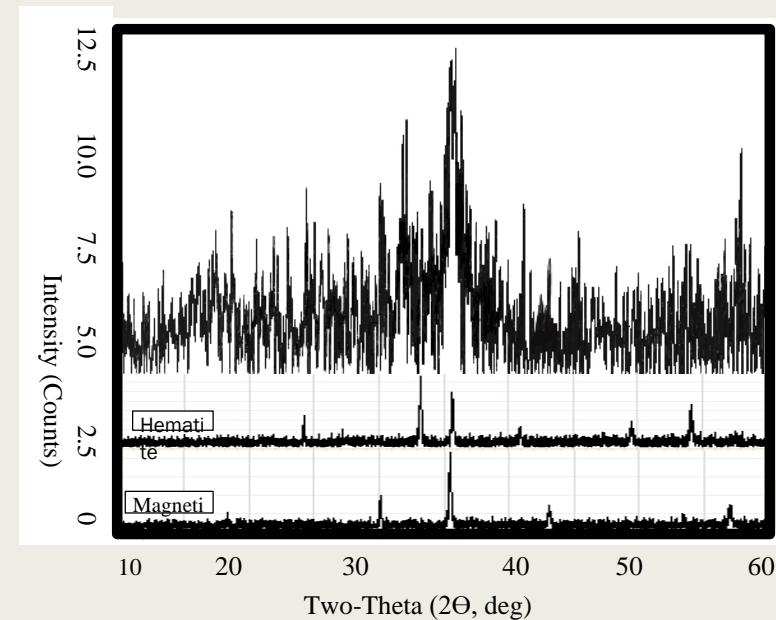
Electrocoagulation of Yogurt Industry Wastewater and the Production of Ceramic Pigments from the Sludge



The treatment of chromium containing wastewater using electrocoagulation and the production of ceramic pigments from the resulting sludge



Using sludge obtained from EC of Tissue paper wastewater as aluminium oxide source for production of polymeric composite



## Some of Articles on Electrocoagulation

1. Umran Tezcan Un, Cansu Filik Iscen, Emre Oduncu, Burcu Akcal Comoglu, Semra Ilhan, Treatment of landfill leachate using integrated continuous electrocoagulation and the anaerobic treatment technique, **Environmental Progress & Sustainable Energy**, Volume 37, Issue 5 , 1668-1676, **2018**, DOI: 10.1002/ep.12850
2. Kagan Eryuruk, Umran Tezcan Un and Ulker Bakir Ogutveren, Electrochemical Treatment of Wastewaters from Poultry Slaughtering and Processing by Using Iron Electrodes, **Journal of Cleaner Production**, Volume 172, 1089-1095, 20 January **2018**.
3. Ersin Aytac, Umran Tezcan Un, Removal of Reactive Scarlet Dye and COD Using Cylindrical Iron Rod Anodes In A Semi-Continuous Reactor, **International Journal of Scientific Research in Science & Technology**, Volume 4, Issue 8, **2018**, Print ISSN: 2395-6011, Online ISSN: 2395-602X
4. Ulker Bakir Ogutveren, Umran Tezcan Un, and Nihal Erginel, Removal of Lead from Water by Electrocoagulation Applying Response Surface Method (RSM) in A Uniquely Designed Rector, **International Journal of Chemical Engineering and Applications**, Vol. 9, No. 3, 109-111 ISSN: 2010-0221, June **2018**
5. Umran Tezcan Un, Ayse Kandemir, Treatment of whey wastewater by electrocoagulation and electro-Fenton methods in batch mode, **Desalination and Water Treatment**, 95, 88-95, **2017**, DOI: 10.5004/dwt.2017.21498
6. Umran Tezcan Un, Suzan Eroglu Onpeker, Emel Ozel, The treatment of chromium containing wastewater using electrocoagulation and the production of ceramic pigments from the resulting sludge, **Journal of Environmental Management**, 200, 196-203, **2017**.
7. Umran Tezcan Un, Seher Topal and Funda Ates "Electrocoagulation of tissue paper wastewater and an evaluation of sludge for pyrolysis", **Desalination and Water Treatment**, Volume 57, Issue 59, **2016**

8. Umran Tezcan Un, S. Eren Ocal, Removal of Heavy Metals (Cd, Cu, Ni) by Electrocoagulation, **International Journal of Environmental Science and Development**, Vol. 6, No:6, **2015**
9. Umran Tezcan Un, Seher Topal, Emre Oduncu, Ulker Ogutveren, Treatment of Tissue Paper Wastewater: Application of Electro-Fenton Method, **International Journal of Environmental Science and Development**, Vol. 6, No:6, **2015**
10. Umran Tezcan Un, Ayse Kandemir, Nihal Erginel, S. Eren Ocal, Continuous electrocoagulation of cheese whey wastewater: An application of Response Surface Methodology, **Journal of Environmental Management** 146, 245-250, **2014**.
11. Umran Tezcan Un, Emre Oduncu, Electrocoagulation of Landfill Leachate with Monopolar Aluminum Electrodes, **Journal of Clean Energy Technologies**, Vol. 2 No.1, January **2014**.
12. Kagan Eryuruk, Umran Tezcan Un, Ulker Bakir Ogutveren, Electrocoagulation in a Plug flow Reactor: The Treatment of Cattle Abattoir Wastewater by Iron Rod Anodes, **Int. Journal of Environmental Research** ., 8(2),461-468, March **2014**.
13. Umran Tezcan Un, Emel Ozel, Electrocoagulation of Yogurt Industry Wastewater and the Production of Ceramic Pigments from the Sludge, **Separation and Purification Technology**, 120, 386-391, **2013**.
14. Umran Tezcan Un, A. Savas Koparal, Ulker Bakir Ogutveren, Fluoride Removal from Water and Wastewater with a Bach Cylindrical Electrode Using Electrocoagulation, **Chemical Engineering Journal**, 223, 110-115, **2013**.
15. Umran Tezcan Un, Ersin Aytac, Electrocoagulation In a Packed Bed Reactor-Complete Treatment of Color and COD from Real Textile Wastewater, **Journal of Environmental Management**, 123 (15), 113-119, **2013**.
16. Umran Tezcan Un, A. Savas Koparal, Ulker Bakir Ogutveren, Hybrid Processes For The Treatment Of Cattle Slaughterhouse Wastewater Using Aluminum And Iron Electrodes, **Journal of Hazardous Materials**, 164 (2-3), 580-586, 30 May **2009**
17. Umran Tezcan Un, A. Savas Koparal and Ulker Bakir Ogutveren, "Electrocoagulation Of Vegetable Oil Refinery Wastewater Using Aluminum Electrodes", **Journal Of Environmental Management**, 90 (1), 428-433, **2009**.