ELECTROCOAGULATION: COD REMOVAL MECHANISM

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Introduction

Electrocoagulation (EC) is electrochemical water and wastewater treatment technology which in its simplest form uses an electrochemical cell where a dc voltage is applied to the electrodes, usually made of Iron or Aluminum, and the electrolyte is the water or wastewater. Current theory of EC has not been able to explain all the phenomena associated with the process, among others the differences in COD removal efficiency in wastewater. In this paper we discuss the facts associated with COD removal using EC and develop a mechanism that explains them. To do so first, a review of the technology is done. Second, the concept related to Oxygen Demand is discussed, next, the results from a pilot plant relative to COD removal efficiency using EC are shown. Last, two set of experiments and a mechanism for COD removal are presented. This mechanism fits data and observations, is congruent with the Iron Pourbaix diagram. Finally the factors affecting COD removal are mentioned.

1.1 EC Comments & challenges

The mechanisms of EC are yet to be clearly understood. There has been little consideration of the factors that influence the effective removal of ionic species, particularly metal ions from wastewaters from this technique.[3].

EC is a complex process with a multitude of mechanisms operating synergistically to remove pollutants from water. A wide variety of opinions exist in the literature for key mechanisms and reactor configurations. A systematic holistic approach is required to understand EC and its controlling parameters.[1]

There has been relatively little effort spent to better understand the fundamental mechanisms of EC, particularly those that could provide design parameters to optimize the performance of this relatively simple and inexpensive technique. [4]

Given the time scale over which EC technology has been utilized it is somehow surprising that the available literature doesn't reveal any systematic approach to EC reaction design and operation. The reason for this failure to drive toward some agreed best solution seems to be the lack of any quantitative understanding of the many interactions that occur within an EC reactor, and in particular the ability to predict the relative importance of these interactions for a given situation. The key driver for of any particular application of this technology has generally been the removal of a specific pollutant. Such centered studies have characterized almost all the published research into EC. Consequently, despite more then a century of application, many of them deemed successful, the science and engineering behind EC reactor design is still largely empirical and heuristic. These studies invariably prove the viability of the technology, but singularly fail to capitalize on its potential by being incorporated within a broad-based understanding of EC technology. [6]

EC is an enigmatic technology. Despite having been widely used for over a century, there appears to be no real consensus on the most appropriate approach for any given application, little in the way of systematic reactor design rules, and almost nothing in the way of a generic a priori modeling approach. The root cause of this situation seems to be that EC is a technology that lies at the intersection of three more fundamental technologies – electrochemistry, coagulation and flotation.

However it is clear from the published literature that what is lacking is a quantitative appreciation of the way in which these technologies interact to provide an optimum EC system so that EC can play a wider role as an accepted and dependable water treatment technology. Research is required to focuses on explaining and quantifying the key interactions and relationships between electrochemistry, coagulation and flotation.

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1.2 COD

COD (Chemical Oxygen Demand) is a measure of the amount of the Oxygen used in the chemical oxidation of inorganic and organic matter present in wastewater. COD is also an indicator of degree of pollution in the effluent, and of the potential environmental impact of the discharge of wastewater in water bodies. COD results do not necessarily correlate to BOD because the chemical oxidant may react with substances that bacteria do not stabilize. Although BOD and COD are not specific compounds, they are considered as conventional pollutants under the federal Clean Water Act, and also they have been widely used by regulatory agencies worldwide to gauge overall treatment plant efficiencies.

1.2.1 Compounds that contribute to COD

Among the compounds that contribute to COD we can find: biodegradable organic compounds, non biodegradable compounds and inorganic oxidizable compounds.

Biodegradable organic compounds. A "biodegradable" product has the ability to break down, safely and relatively quickly, by biological means, into the raw materials of nature and to disappear into the environment. The biodegradable compounds can be dissolved or suspended solids, colloids, organic matter, etc.

Non-biodegradable compounds. Sometimes non-biodegradable compounds are also called xenobiotics. They are not capable of being broken down naturally into environmentally harmless products. They are released into the environment in higher amounts than are present in nature. These compounds, for example, pesticides, herbicides, halogenated solvents, chlorinated aromatic hydrocarbons, chlorinated aliphatic hydrocarbons and toxins, are often very toxic or recalcitrant because of their molecular structure, excessive molecular size, their very stable bonds (C–Cl), and their limited bioavailability (*e.g.*, hydrophobic compounds bound into organic matter are not available to microbes).

Inorganic oxidizable compounds. This group is comprised of metal/metalloid cations such as iron, arsenic; and anions such as cyanides, nitrites, sulfites, and sulfides.

These three kinds of compounds can also be classified as follows, and this classification is more convenient for the electrocoagulation process.

Organic compounds, which encompasses: Suspended solids and liquids such as micro organisms, emulsions, colloids, and fat, oil & grease (FOG); Miscible liquids such as alcohols, benzene, glycerin, oils, etc.; and Dissolved solids and liquids such as acids, salts, sugars, etc.

Inorganic compounds, mainly dissolved such as metals like Fe, metalloids like As, and some anions such as CN, NO_2 , SO_3, and S.

2. Electrocoagulation mechanism for COD removal.

This study is based on the tests that Kaselco Electrocoagulation, a manufacturer of EC units, has been doing at its laboratory for its consumers from 1997 to 2005. Most of the tests are for wastewater treatment, and complete analysis of water not always known.

2.1 Removal efficiency

Removal efficiency for Organic Compounds, BOD and COD from the Kaselco available data is summarized in Table I (consider number of tests for standard error).

Table I. Organic compounds Removal Efficiency (%) with EC.

	# of tests	Min. removal Effic. (%)	Max. removal Efficiency (%)	µ mean	σ Std. dev.
Fecal Coliform	9	88.90	100.0	98.20	3.60
Surfactants	1	96.16	96.16	96.16	0.00
TPH	4	67.90	99.80	91.0	15.40
Turbidity	38	32.40	100.0	82.20	22.90
Clarity	17	31.10	100.0	81.10	21.80
TBX	7	63.40	93.30	76.00	11.20
Fats, Oil & Grease	9	0.3	100.0	75.4	24.8
TSS	18	7.40	100.0	73.30	31.80
MTBE	11	15.0	95.90	47.00	25.50
Methyl Chloride	2	28.10	65.60	46.90	26.60
BOD	49	0.00	98.40	40.70	27.10
COD	65	0.50	86.40	38.90	27.30
Acetone	3	20.70	33.60	28.10	6.60
TOC	4	8.30	22.50	14.60	6.60
TKN	5	3.60	28.80	13.60	10.30
2-Butanone	2	3.90	1410	9.0	7.20

It can be seen from the results that there is an extremely high variability in removal efficiency of organic compounds. This is one of the reasons why EC hasn't always been accepted as a conventional technology and why it is considered enigmatic. COD removal efficiency may vary from nearly 0% to a surprising 100% depending on the solution tested. Questions arise immediately first; why can EC work extraordinarily well in some cases and fail completely in others; second, why are some compounds more easily removed than others?

A mechanism for EC will have to explain differences in COD removal as well as fit the current EC theory. To reach this goal we have to take a look at the current theory of EC, and review some of the proposed mechanism:

2.2 Electrocoagulation Mechanism.

Current theory of EC states that it involves several successive stages:
1) Generation of metal ions.
*2) Hydrolysis of metal ions and generation of metal hydroxides and polyhydroxides***.** This is beyond question, it has been studied and explained for coagulation process in water treatment.
3) Water is also electrolyzed in a parallel reaction, producing small bubbles of Oxygen at anode and Hydrogen at the cathode. Although the presence of magnetite and maghentite identified in EC sludge

can suggest Oxygen evolution at the anode this does not happen. To examine whether there is O_2 evolution, an EC cell was prepared using two cylindrical iron electrodes supported on a PVC stand and covered with graduated cylinders full of water to observe the displacement of water if any gas is generated.

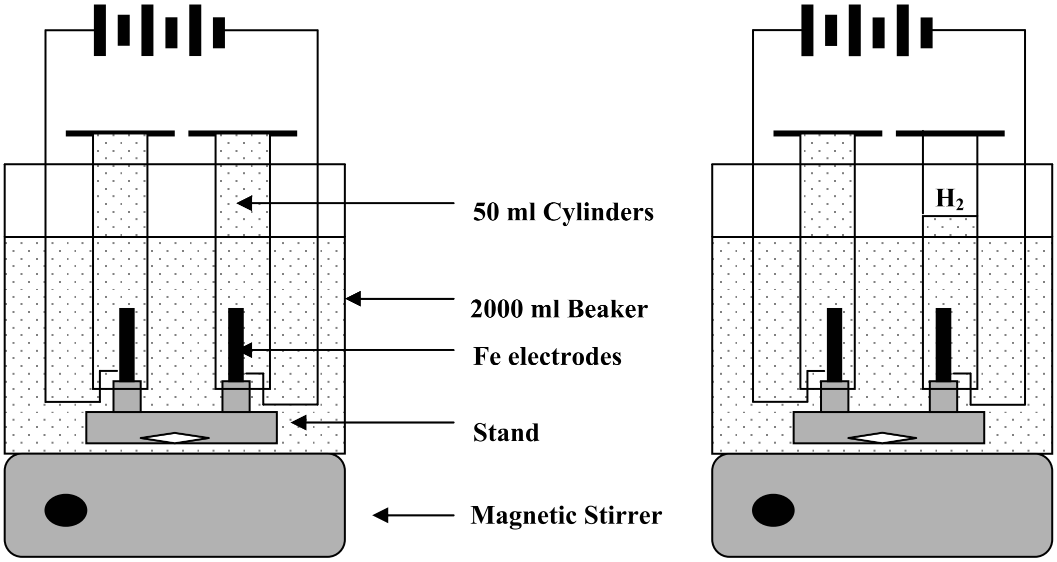

Figure 1. Diagram of the EC reactor used to probe oxygen evolution at the cathode

The solution used had 170 ppm of $ZnCl_2$ and 1000 ppm of NaCl to increase the conductivity of water. Electrodes were connected to a 50 Volts DC source. The experiment began at a pH of 5.2 and continued up to a pH of 10.74. The experiment showed that there is no oxygen evolution at the anode using iron electrodes, but hydrogen evolution at the cathode. Diagram of the reactor in Figure 1.

4) Destabilization of the contaminants, particulate suspension, breaking of emulsions, and aggregation of the destabilized phases to form flocs. This part relative to colloids and suspended matter can be accepted because suspended solids and colloids in small quantities are not a problem for EC.

5) Current theory of EC consider that chemical reactions and precipitation can occur during the EC process or that other cation or the hydroxyl ion (OH) form a precipitate with the pollutant.

In the Electrocoagulation cell the reactions are:

<table>
<tr><th>pH</th><th>Anode</th><th>Cathode</th></tr>
<tr><td>water & pH <5</td><td>$Fe \rightarrow Fe^{+2} + 2\ e^-$
$2Fe^{+2} \rightarrow 2Fe^{+3} + 2\ e^-$
In fact Iron also undergoes hydrolysis
$Fe + 6H_2O \rightarrow Fe(H_2O)_4(OH)_{2\ (aq)} + 2H^{+1} + 2e^{-1}$
$Fe + 6H_2O \rightarrow Fe(H_2O)_3(OH)_{3\ (aq)} + 3H^{+1} + 3e^{-1}$</td><td>$2H^+ + 2\ e^- \rightarrow H_{2(g)}\uparrow$</td></tr>
<tr><td colspan="3">Electrochemistry depends on thermodynamics and kinetics. The rate of reaction will depend on the removal of $[H^+]$ via H_2 evolution, this reaction will proceed fast for low pH values for a strong acid. For a weak acid the rate will depend on the pKa of the acid. Electro neutrality principle has to be kept in any step.</td></tr>
<tr><th>pH</th><th>Anode</th><th>Cathode</th></tr>
<tr><td>5 <pH< 7</td><td>$Fe(H_2O)_3(OH)_{3\ (aq)} \rightarrow Fe(H_2O)_3(OH)_{3\ (s)}$
More hydrogen evolution and Fe(III) hydroxide begin to precipitate floc with yellowish color.
Formation of rust: $2Fe(H_2O)_3(OH)_3 \leftrightarrow Fe_2O_3\ (H_2O)_6$</td><td>$2H^+ + 2e^- \rightarrow H_{2(g)}\uparrow$</td></tr>
<tr><td>6 <pH< 8</td><td>$Fe(H_2O)_3(OH)_{3\ (aq)} \rightarrow Fe(H_2O)_3(OH)_{3\ (s)}$
$Fe(H_2O)_4(OH)_{2\ (aq)} \rightarrow Fe(H_2O)_4(OH)_{2\ (s)}$
Hydrogen evolution continues and precipitation of Fe(II) hydroxide also occurs presenting a dark green floc. The pH for minimum solubility of Fe(OH)n is between 7 – 8
Formation of rust. Oxides are dehydrated hydroxides
$2Fe(OH)_3 \leftrightarrow Fe_2O_3 + 3H_2O$
$Fe(OH)_2 \leftrightarrow FeO + H_2O$
$2Fe(OH)_3 + Fe(OH)_2 \leftrightarrow Fe_3O_4 + 4H_2O$
Polymerization of iron oxyhydroxides to form the floc.</td><td>$2H^+ + 2e^- \rightarrow H_{2(g)}\uparrow$</td></tr>
<tr><td colspan="3">This mechanism follows the Pourbaix diagram, Figure 2 for hydroxides, and also the characterization of EC products made by Parga et al. Conditions throughout the cell are not constant. Potential, concentrations, species and pH are changing. It can be said that in the iron Pourbaix diagram we are moving to the right in a region parallel to the hydrogen evolution line as highlighted in Fig 7</td></tr>
<tr><td>pH > 8</td><td colspan="2">$Fe + 6H_2O \rightarrow Fe(H_2O)_4(OH)_{2\ (aq)} + H_{2(g)}\uparrow$
$Fe + 6H_2O \rightarrow Fe(H_2O)_3(OH)_{3\ (aq)} + 1\ ½\ H_{2(g)}\uparrow$
Sludge and rust generation continues. In fact iron oxides are dehydrated iron hydroxides, and some of this oxidation occurs on the surface of the floated sludge. It can also occur during filtration and preparation of the sample.</td></tr>
</table>

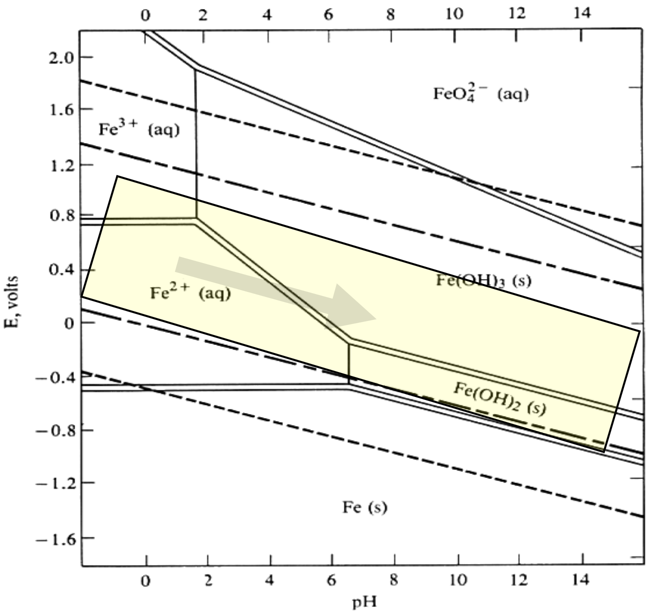

Figure 2. Fe Pourbaix Diagram, showing the region and direction in which the EC process proceeds.

2.3 Experiments and results.

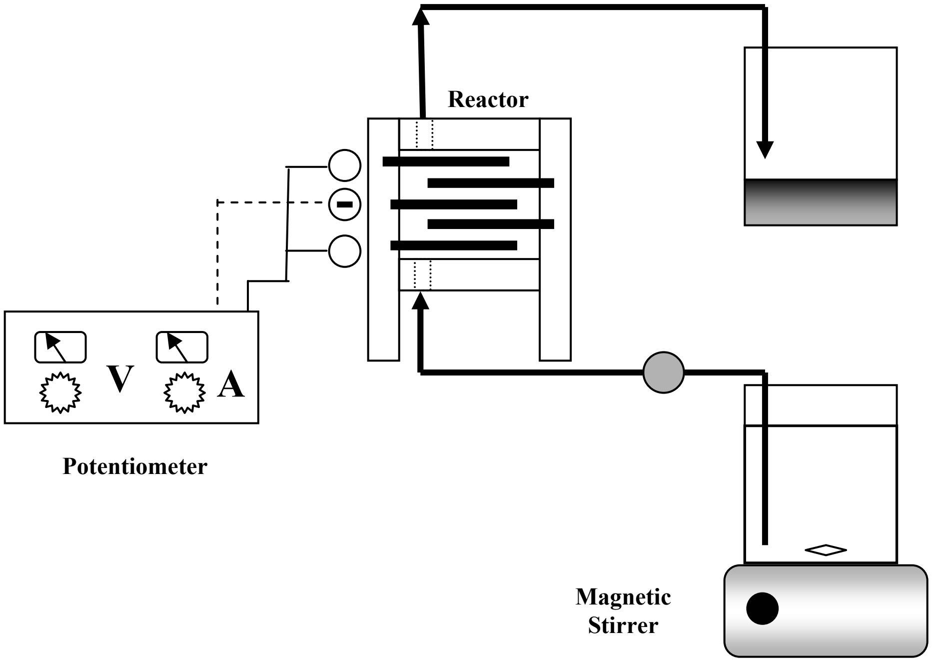

Figure 3. Diagram of the bench reactor

For a first set of experiments the following equipment was used: a Kaselco electrocoagulation bench unit (Fig 3), which has a rectifier with capacity up to 50 Volts or to 10 Amps and a peristaltic reversible pump with adjustable flow, a Corning pH meter 320, a Corning conductivity meter 441, a Perkin Elmer Atomic Absorption Spectroscopy AAnalyst 300 SE 3953, and reagent grade chemicals. The COD determinations were made by B-Environmental Laboratory in Victoria TX. Results are presented in Table II.

The electrode plates have dimensions of 4 x 4 x ¼" for the exposed area. They can be made of Fe, Al or Ti. The separation between plates is ≤ ½". 2.2 L of water sample is passed trough the reactor twice, and this is considered one pass in relationship to the full scale system. Complete treatment of wastewater can take more than one pass. (one pass takes approximately 6 minutes in the bench test).

Another set of experiments was conducted using a Beaker size electrochemical cell. Materials and equipment used were: 400 ml sample, rectangular iron electrodes with dimensions 3 x 6 cm, and with a submerged area of 12 cm^2 each, a 12 volts Interstate battery, an Ohmite potentiometer, a Fisher magnetic stirrer, an Oakton series 10 pH meter, a Cole Parmer conductivity meter, and reagent grade chemicals. Current was measured using a Cen Tech multimeter in series, and the potential with a Cen Tech multimeter connected in parallel. COD determinations were made using standard methods with: a DRB 200 Hach COD Reactor for digestion of the sample, and a DR 3000 Hach spectrophotometer for colorimetric determination. Electrodes were properly scrubbed, washed and rinsed prior to each experiment to make their surface clean and free from passive oxide layers. Results are presented in Table III.

Table II Results for 1st set of experiments. P Passes, I initial, F final, R removal.

Subst.	**gr/L or ml/L**	**# of t**	**pH**		**Final Fe ppm**	**BOD (mg/L)**			**COD (mg/L)**		
			I	**F**		**I**	**F**	**R (%)**	**I**	**F**	**R (%)**
EDTA	3	2	2.96	10.24	52.85	182	256	-40.7	173.5	302.5	-74.4
Acetic Acid	2	6	3.01	7.64	563.0	1599	1657	-3.6	2134	2162	-1.3
IPA	1,5	2	4.5	10.98	0.069	1599	1447	9.51	2498	2410	3.52
Sugar	2	1	4.59	11.19	0.178	1539	1254	18.5	2272	2120.5	6.7
Sodium Oxalate	2	1	5.98	11.6	0.045	188	116.5	38	216	182	15.7
Milk	3	1	5.72	10.92	0.029	364	93.5	74.3	572	148	74.1
Oxalic Acid	2	3	2.07	7.12	76.6	146	27	81.5	216	5	97.7

Table III. Results for 2nd set of experiments

Substance	**Residence time (min)**	**COD (mg/L)**		
		Initial	**Final**	**(%) Removal**
Acetic Acid	60	961	1083	-12.7
Glucose	60	983	1012	-2.95
Lactose	60	969	948	2.17
Phenol	60	1158	1125	2.85
Citric Acid	60	1081	515	52.36
Salicylic Acid	60	982	370	62.32
Tartaric Acid	90	1027	135	86.85
Oxalic Acid	90	1029	131	87.27

2.3.1 Combined results.

In table 4 the combined results of the 2 set of experiments relative to COD removal are presented. Initial iron in the samples was 0 ppm. From these results it can be seen that depending on the organic compounds present in water and after the EC process, COD can be increased, remain nearly the same, be partially removed, or be almost completely removed. From these results we can determine the EC COD removal mechanism.

3 Discussion and conclusions

Increased COD

Compounds (usually acids) which react with Fe(II) or Fe(III) to form soluble products will remain in solution. This can be concluded for the final iron concentration and the pH increment. This is even more pronounced in the case of sequestrants or complexing agents such as EDTA. When they react, mainly with Fe(II), in the corresponding experiment, we can say that most of the iron was Fe(II) because the final pH was 10.24 (see Table II), and in cases such as this COD can be increased due to further oxidation of Fe(II) to Fe(III).

Table IV. Combined results of the 2 set of experiments

Substance	**In water**	**Reacts with Fe(II)**	**Reacts with Fe(III)**	**COD removal (%)**	**Final Fe (ppm)**
EDTA	Soluble	To form soluble compound	To form soluble compound	-58.5 to -87.5	52.85
Acetic Acid	Soluble	To form soluble compound	To form soluble compound	-3.4 to 0.8	563
Glucose	Soluble	No	No	-3.2 to -2.7	
Lactose	Soluble	No	No	1.3 to 2.9	
Phenol	Miscible	No	No	2.8	
IPA	Miscible	No	No	2.7 to 4.4	0.069
Sugar	Soluble	No	No	3.6 to 9.6	0.178
Sodium Oxalate	Soluble	*	*	11.8 to 19.3	0.045
Citric Acid	Soluble	**To form insoluble compound**	To form soluble compound	51.9 to 52.8	
Salicylic Acid	Soluble	**To form insoluble compound**	To form soluble compound	61.8 to 62. 8	
Tartaric Acid	Soluble	**To form insoluble compound**	Decomposes in water	86.7 to 86.9	
Oxalic Acid	Soluble	**To form insoluble compound**	To form soluble compound	87.3 to 87.7	76.6
Milk	Suspension	No	No	73.7 to 74.5	0.029

COD not removed

Soluble and miscible compounds that do not react with Fe(II) or Fe(III) will not be removed with

EC and they will remain in solution. This is the case of glucose, lactose, IPA, phenol, sugar and similar compounds. A small amount can be adsorbed or absorbed on the floc and consequently be removed incidentally.

COD partially removed

* Sodium oxalate and similar organic salts are another case. The EC process generates Fe ions that hydrolyze to form $Fe(OH)_2$ and/or $Fe(OH)_3$, together with H^+ ions, since Fe(II) and Fe(III) are more acidic than Na^+ then $(OH)^-$ ions will preferentially stay with them to form insoluble iron hydroxides and the acetate ion will be only removed in a low proportion.

Compounds which react with Fe(II) or Fe(III) to form insoluble compounds will be partially removed. This is the case of citric, salicylic, tartaric and oxalic acids. COD removal efficiency for these compounds will depend on the final pH.

COD highly removed

It can be expected that compounds that react with both Fe(II) and Fe(III) to form insoluble compounds will be completely removed.

On the other hand, from table I it can be seen that suspended solids and liquids, in small amounts, such as fecal coliforms, turbidity, fats oil & grease, suspension such as milk, and TSS are not a problem for EC and are easily removed. This is due to the in situ generated coagulants. The portion not removed will be the soluble portion of those parameters that does not react with Fe(II) or F(III) to form insoluble compounds.

In some cases Al electrodes show higher COD removal efficiencies at lower pH values for two reasons, the first a difference of Iron, Aluminum only has one oxidation state, so when an organic compound reacts with aluminum to form an insoluble compound it will react almost completely, and second the solubility of Aluminum Hydroxide [$Al(OH)_3$] has its minimum at a lower pH, close to 4. Anyway every compound that contributes to COD is different, and also every wastewater. It will be better to try both, Fe and Al electrodes and even a combined system in order to get the best results.

EC can be considered as an accelerated corrosion process that follows the Pourbaix diagram. An EC mechanism for COD removal was developed. This model fits data and observation of Kaselco tests. It is also congruent with the iron Pourbaix diagram, the Solubility diagram, and with the characterization of EC products, and fully explains the causes of the great variability in the results for COD removal efficiency. Summarizing, we can say that COD removal efficiency and its variability will depend on the: formation of floc, which usually occurs at values of pH higher than 7.5 for Iron electrodes, reactivity of organic compounds with Fe(II) and Fe(III), the solubility of the compounds formed, the final pH (especially for acidic compounds final pH is an important factor for COD removal), the pH increment, and consequently on the acidity of the wastewater rather than on the initial pH, and on the electrodes material.

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