

# Chapter 5: Background on advanced oxidation processes

Advanced oxidation processes are a series of methods that produce highly oxidative radicals to degrade persistent molecules. Several techniques are involved and they can be broadly divided in two: 1) methods that do not use radiation and 2) methods that use radiation (photochemical). Table 5-1 shows examples of advanced oxidation processes (AOPs) from each category.

**Table 5-1.** Classification of advanced oxidation processes [Domènech *et al.*, 2004]

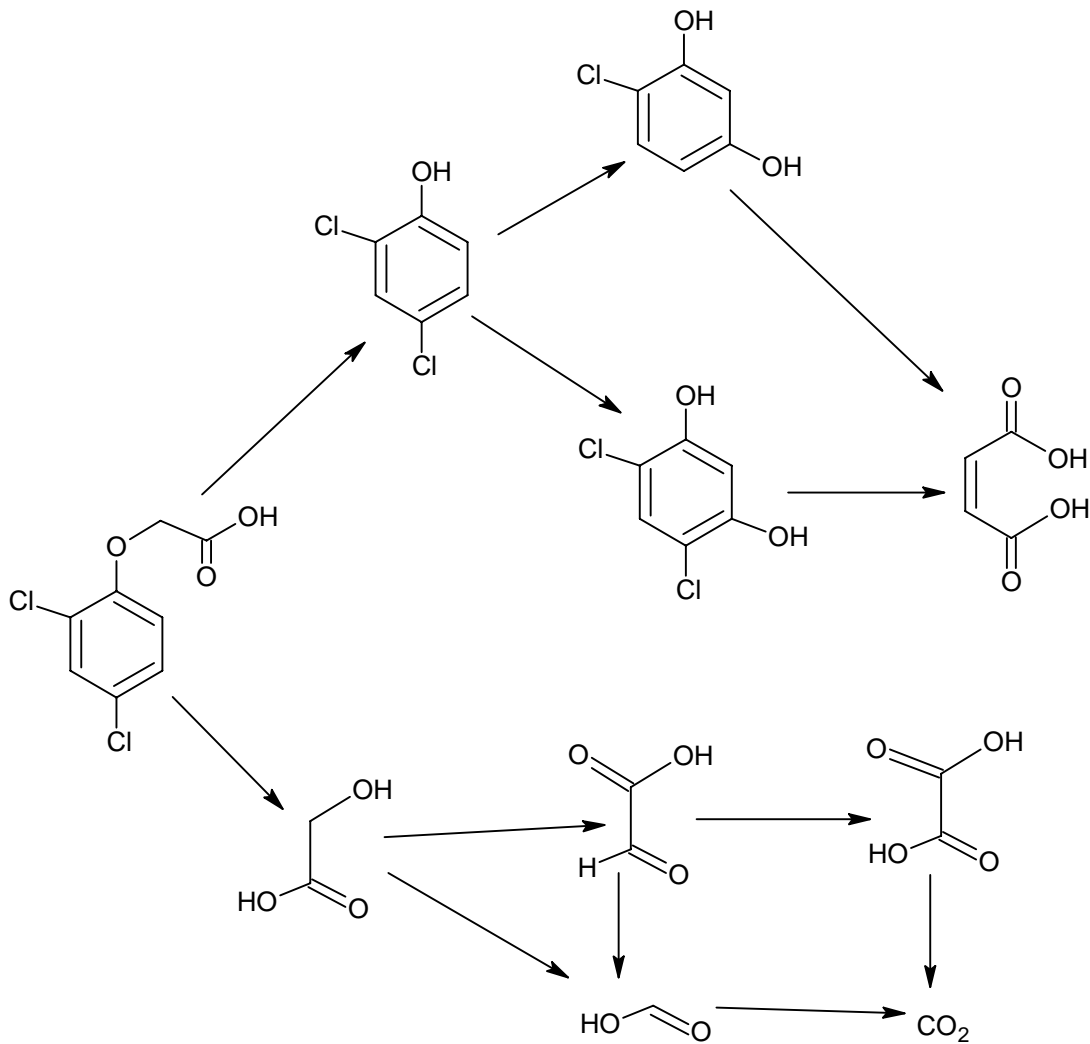
<b>Non-photochemical processes</b>	<b>Photochemical processes</b>
Ozonation in an alkali medium ( $O_3/OH^-$ )	Sub and supercritical water oxidation
Ozonation with hydrogen peroxide ( $O_3/H_2O_2$ )	Water photolysis in vacuum ultraviolet (UUV)
Fenton and related processes ( $Fe^{2+}/H_2O_2$ )	UV/hydrogen peroxide
Electrochemical oxidation	UV/ $O_3$
Radiolysis $\gamma$ and treatment with electron beam	Photo-Fenton $\gamma$ related processes
Non-thermal plasma	Heterogeneous photocatalysis
Electrohydraulic-ultrasound discharge	

Many of the AOPs use the  $\cdot OH$  radical as their primary tool in the breaking down of recalcitrant molecules. The redox or oxidation potential is a measure of the voltage to which electrons

outside a system would have to be exposed to equal the electrochemical energy per mole that the electrons have in the system of interest [Benjamin, 2002]. Thus this parameter is an estimation of the energy of chemical species expressed in volts. The hydroxyl radical has the second largest redox potential (2.80 V at 25°C) (although Bard (1985) reports it at 2.38 V and Stanbury (1989) at 2.72 V) with the most potent being fluorine (3.03 V at 25°C) and over the second choice for oxidation, O<sub>3</sub> (2.07 V at 25°C). Thus this species is able to attack most organic compounds and it reacts 10<sup>6</sup>-10<sup>12</sup> times faster than ozone [Domènech et al, 2004]. In order to be efficient, AOPs must generate high concentrations of ·OH radicals in a steady state [Domènech et al, 2004]. Some AOPs (heterogeneous photocatalysis or radiolysis) use chemical reducers for species not subject to oxidation, like metallic ions or halogenated compounds. Many of the products mineralized by AOPs are toxic to microorganisms, which makes these processes suitable for pre-treatment of water that can afterwards be treated by conventional biological technologies.

For pesticides, Mabury and Crosby (1994) have reported the order or relative reactivity toward hydroxyl radicals for several pesticides: carbaryl > carbofuran > mephanac > 2,4-D > propanil > molinate > atrazine > hexazinone > quinclorac.

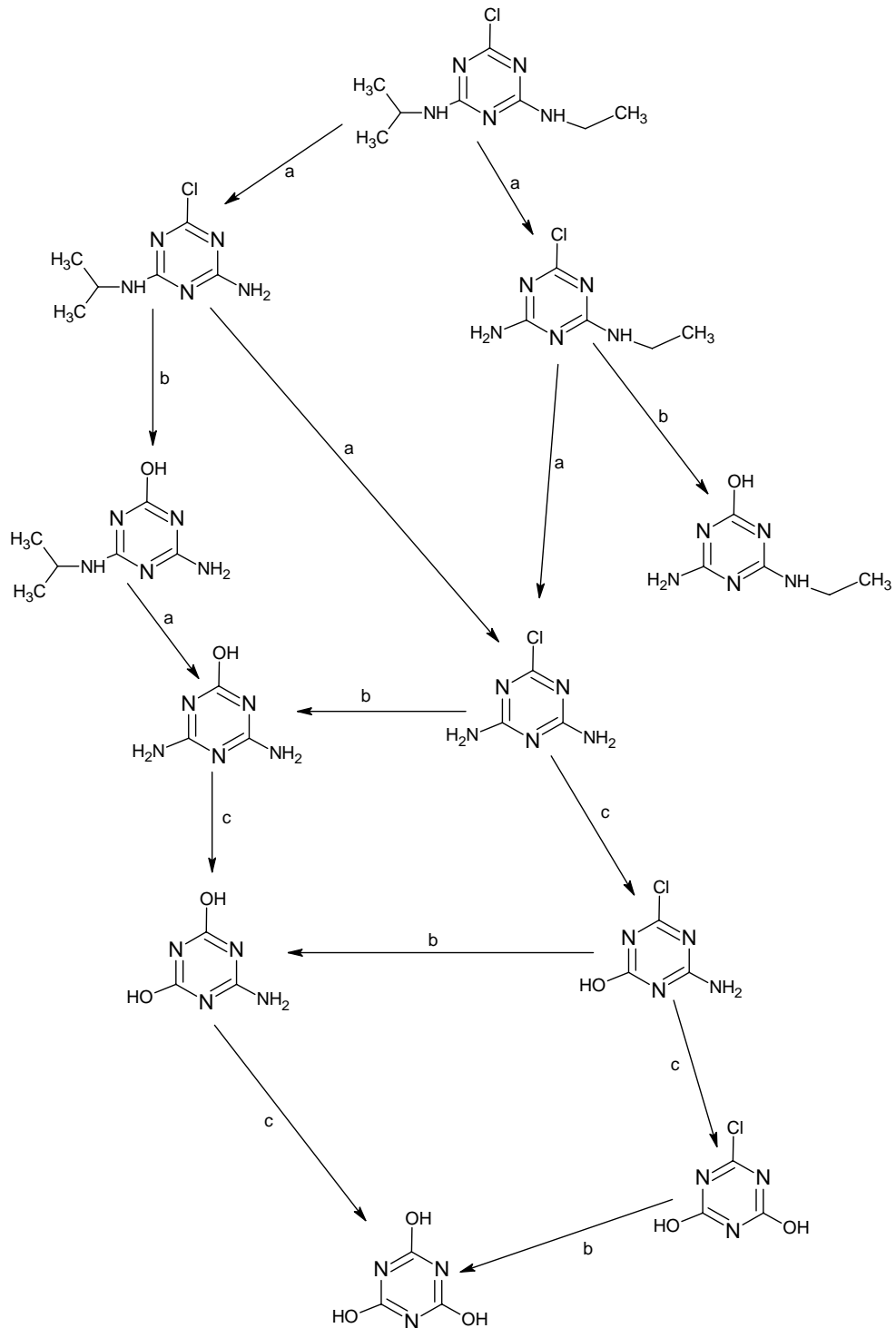
Some degradation pathways have been offered for 2,4-D and atrazine. Presumably, all AOPs would present similar rupture routes, since most are based on the hydroxyl radical to begin breakup. Figures 5-1 and 5-2 are proposed pathways for the mineralization of 2,4-D and atrazine.



**Figure.5-1.** Proposed degradation pathway of 2,4-D by ozonolysis. [Ikehata and El-Din, 2005]

This model proposed by Ikehata and El-Din (2005) was studied using O<sub>3</sub> as the ·OH radical inductor. The first step is the separation of aromatic and aliphatic components of 2,4-D. CO<sub>2</sub> is obtained after continuous oxidation of the aliphatic chain. Regarding the aromatic ring, different oxidation pathways substitute Cl for OH and eventually lead to the breakup of the ring.

For atrazine, Pelizzetti *et al.* (1990-1992) have proposed the following sketch to describe its mineralization.



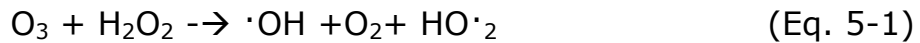
**Figure 5-2.** Proposed degradation pathway for atrazine by heterogeneous photocatalysis. [Pelizzetti et al, 1990-1992]

Pelizzetti *et al.* (1990-1992), identify different chemical reactions by letters. All arrows labeled "a" show lateral alkyl chain oxidation, "b" refers to dechlorination and "c" indicates deamination. As far as the bibliographic research found, cyanuric acid is the last species known for the mineralization by AOPs of atrazine. Cyanuric acid is toxic, but its degradation has been achieved by stable mixed bacterial cultures [Mandelbaum *et al.*, 1993].

## **5.1 Non-photochemical processes**

### **5.1.1 O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>**

Ozone is a powerful oxidant, being the fourth most reactive species in Domènech's list in Table I [Domènech *et al.*, 2004]. It has bactericidal properties and is commonly used for drinking water disinfection. Ozone may be formed *in situ* by supplying electrical current to oxygen and it is an unstable species, thus its life is short. Since O<sub>3</sub> is a gas injected to a liquid, mass transfer resistances must be acquainted for. Used with hydrogen peroxide, the combined oxidizing power may result in rapid mineralization of compounds. It is an expensive process, but it can treat very diluted organic compounds (ppb). It works well in a pH range of 7-8 and the optimal molar relationship O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> is 2:1 [Domènech *et al.*, 2004]. Ozonation of organic compounds may go through two types of pathways, molecular ozone reactions (ozonolysis) or hydroxyl radical reactions. The path taken by the reaction depends on pH. At low pH ozonolysis is favored, while at pHs > 8 ozone molecules are decomposed into free radicals,  $\cdot\text{O}_2^-$  and  $\text{HO}\cdot_2$ , which in turn produce the hydroxyl radical  $\cdot\text{OH}$  [Ikehata and El-Din, 2004]. The general equation as written by Domènech is

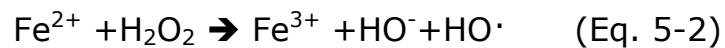


There are commercial equipments available that use this technology, which is suitable for water with high-turbidity where radiation would be impeded.

### 5.1.2 Fenton and Fenton-like techniques

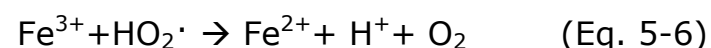
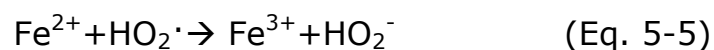
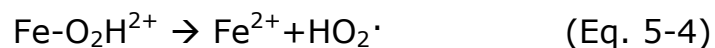
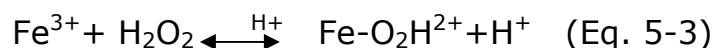
The Fenton process is a useful technique to treat wastewater with high concentration of recalcitrant compounds due to its efficiency in producing hydroxyl radicals. It is based on the coupling of a transition metal with an oxidant. Fenton couples iron(II) with hydrogen peroxide.

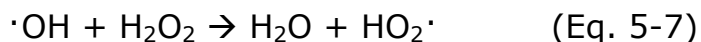
Domènech *et al.* (2004) suggested that  $\cdot\text{OH}$  was formed by the following general reaction:



Hydroxyl radical could then react through one of two pathways: oxidation of Fe(II) or the attack of organic matter. The process is limited to pH less than 3, and causes some iron sludge that needs post-treatment [Jeong and Yoon, 2005].

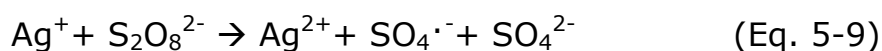
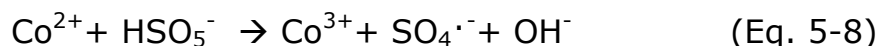
Pignatello (1992) describes the reactions that allow the regeneration of  $\text{Fe}^{2+}$ . The more oxidized species  $\text{Fe}^{3+}$  acts as a catalyst for the decomposition of peroxide to  $\text{O}_2$  and  $\text{H}_2\text{O}$ , regenerating  $\text{Fe}^{2+}$  for the continued Fenton reaction:





When excess  $\text{H}_2\text{O}_2$  is used,  $\text{Fe}^{2+}$  is in a lower concentration than  $\text{Fe}^{3+}$  since reaction 5-5 is slower than reaction 5-2 [Pignatello, 1992].

There are, however, other compounds that are used as transition metal and oxidants. Anipitakis and Dionysiou (2004) reported the testing of Ag(I), Ce(III), Co(II), Fe(II), Fe(III), Mn(II), Ni(II), Ru(III) and V(III) coupled with three oxidants; hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), potassium peroxymonosulfate ( $\text{KHSO}_5$ ) and potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ). They conclude that the most efficient metals for the activation of each oxidant are: Fe(II) and Fe(III) for  $\text{H}_2\text{O}_2$ , Co(II) for  $\text{KHSO}_5$  and Ag(I) for  $\text{K}_2\text{S}_2\text{O}_8$ . The reactions concerning the systems Co- $\text{KHSO}_5$  and Ag- $\text{K}_2\text{S}_2\text{O}_8$  are presented:



The Co- $\text{KHSO}_5$  system operates well at a wider pH range, (2-8), while the Ag- $\text{K}_2\text{S}_2\text{O}_8$  needs to work under pH of 3 to avoid metallic precipitation and sludge formation [Anipitakis *et al.*, 2004]. The above mentioned authors reported that the  $\text{SO}_4^{\cdot-}$  radical has a stronger oxidizing power than  $\text{HO}\cdot$  at elevated pH (>5) with a redox potential between 2.5 and 3.1 V.

### 5.1.3 Electrochemical oxidation

By applying electrical current to water the hydroxyl radical is formed, which can then oxidize organic matter.

Domènech *et al.* (2004) gives two equations that describe the process:



Suggested electrical current is between 2 and 20 A [Domènech *et al.*, 2004] and the material for the electrodes determines the  $\cdot\text{OH}$  production rate. Quiroz *et al.*, (2005) report that depending on the electrode material, the oxidation mechanism proceeds through either the preliminary introduction of oxygen into the oxide lattice, which results in a change of the oxidation state of the metal ( $\text{IrO}_2$  and  $\text{RuO}_2$  electrodes) or the electrochemical combustion, that yields  $\text{CO}_2$  by a direct surface oxidation of the organic compound ( $\text{SnO}_2$  and  $\text{PbO}_2$  anodes).

## **5.2 Photochemical processes**

Photocatalysis has been defined by Plotnikov (1936) as the acceleration of a photoreaction by the presence of a catalyst. On the other hand, photocatalysis has been viewed as the enhancement of catalytic processes by their exposition to radiation. Many authors have assayed the difference in reaction efficiencies and velocities under dark and radiated conditions. In this sense we have photo-electrochemical oxidation (Enea *et al.*, 1999; Boye *et al.*, 2003), photo-Fenton and Fenton-like processes (Anipsitakis and Dionisyou, 2003; Jeong and Yoon, 2005; Pignatello, 1992; Sun and Pignatello, 1993;), photo-ozonolysis (Müller *et al.*, 1998), and photo-hydrogen peroxide (De Laat *et al.*, 1999).

### **5.2.1 UV/ $\text{H}_2\text{O}_2$**

In systems where one strong oxidant is exposed to radiation, the principle is that energy from light is strong enough to



break the bonds between molecules and thus generate radicals. Oxidants must be photosensitive for this degradation to occur. Domènech *et al.* (2004), has proposed the following equation describing the rupture of H<sub>2</sub>O<sub>2</sub> with a  $\lambda=254$  nm:



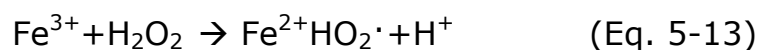
Photolysis of hydrogen peroxide is achieved using mercury vapor UV lamps of low or moderate pressure. Generally,  $\lambda=254$  nm lamps are used although maximum H<sub>2</sub>O<sub>2</sub> absorbance occurs at  $\lambda=220$  nm. When there is excess peroxide and high  $\cdot\text{OH}$  concentrations, there are competing reactions between the  $\cdot\text{OH}$  that can lower overall efficiency [Domènech *et al.*, 2004].

### 5.2.2 Photo-Fenton and related processes

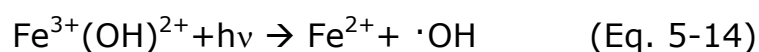
Recalling the basic equation of the Fenton process:



This equation tells us that iron(II) oxidizes to iron(III), producing a hydroxyl radical. Another important step in the Fenton process is iron(II) regeneration through equations 5-2 to 5-6, summarized as:



This regeneration is slow and the use of radiation greatly increases the speed of reaction as:



The reason for increased velocity is that  $\text{Fe}(\text{OH})^{2+}$ , the main Fe species dissolved in water, is photosensitive and absorbs light at wavelengths of 400nm or less [Anipitakis and Dionysiou., 2004] .

The increased degradation velocity of organic molecules by submitting Fenton and Fenton-like reagents to UV light has been extensively discussed (Anipitakis and Dionysiou, 2004, Sun *et al.*, 1993, Kaichouh *et al.*, 2004). The enhancement of the velocity of reaction seems to be comparable to other Fenton-like systems. Anipitakis and Dionysiou (2004) report that degradation of 2,4-dichlorophenol, UV/Co/KHSO<sub>5</sub> was twice as fast as Co/KHSO<sub>5</sub>, and for UV/Ag/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> complete degradation was achieved after 1 hour while Ag/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> could only attain 12% degradation.

### 5.2.3 Heterogeneous photocatalysis

In heterogeneous photocatalysis, the catalyst is in a different phase, usually solid. The chemical reaction is then a surface phenomenon, and adsorption mechanisms and surface area become important parameters. Catalysts used are semiconductor metallic oxides or salts, and few have been found useful under UV lamp or solar conditions. Moreno (2005) mentions some of these: TiO<sub>2</sub>, ZnO, CdS, iron oxides, WO<sub>3</sub>, ZnS. Each catalyst has its own characteristics and operation ranges, and selection depends upon the radiation source and organic compound to degrade. The more deeply studied catalysts are the wide gap metallic oxides, being titanium dioxide (TiO<sub>2</sub>) the most studied [Moreno, 2005]. Titanium dioxide is a fine powder and has been used in supported systems or in suspension, forming two phases.

When a semiconductor is excited with light of shorter wavelengths than the band gap, electron-hole pairs are formed. These may recombine (releasing heat) or may migrate to the surface of the semiconductor where they can undergo redox reactions with

molecule and ions near the surface. The positively charged holes react at great speed with water to produce hydroxyl radicals, which in turn, attack organic molecules. The following equations summarize the process  $\text{TiO}_2$  undergoes in the production of  $\cdot\text{OH}$  [Halmann, 1996]:



Turchi and Ollis (1990) put forward four possible general mechanisms for the photodegradation of organic molecules by radiated aqueous  $\text{TiO}_2$ :

1) While both the  $\cdot\text{OH}$  radical and the organic molecules are adsorbed on the  $\text{TiO}_2$  surface.

2) Between an adsorbed organic molecule and a non-bound  $\cdot\text{OH}$  radical (free in solution).

3) Between an adsorbed  $\cdot\text{OH}$  radical and a free organic molecule hitting the catalyst surface.

4) Between a free  $\cdot\text{OH}$  radical and a free organic molecule in solution.

### 5.3 Figures-of-merit

A figure-of-merit is a numerical quantity based on one or more characteristics of a system or device that represents a measure of its efficiency. Usually figures-of-merit are used to compare systems that result in the same effect and depend on certain common variables.

Bolton *et al.* (2001) have suggested four figures-of-merit based on the amount of energy a cubic meter of water needs to achieve a certain level of pollutant mineralization. The authors organized their proposal by energy source (electrical, solar) and influent contaminant concentration (high, low). They describe zero order kinetic behavior ( $\frac{dC}{dt}=k$ ) when dealing with high concentrations and first order kinetic behavior ( $\frac{dC}{dt}=kC$ ) for lower ones. Electrical figures-of-merit are offered first and are given in units of kilowatts-hour, since the cost of electricity is the major investment associated with these types of *AOPs*. Solar based figures are described next. They have units of square meter per cubic meter per order, since collector area is the main capital cost for these.

#### 5.3.1 Electric energy per mass

It is suitable for use with electric energy driven systems when the contaminant concentration is high (i.e. > 100 mg/L). It corresponds to a zero order kinetic behavior. Electric energy per mass ( $E_{EM}$ ) is the electric energy in kilowatt-hours (kWh) required to reduce the concentration of a unit mass of a contaminant  $C$  in water or air. Equations 5-18 and 5-19 describe  $E_{EM}$ :

$$E_{EM} = \frac{P}{FM(c_i - c_f)} \quad (\text{Eq. 5-18})$$

$$E_{EM} = \frac{Pt1000}{VM(c_i - c_f)} \quad (\text{Eq. 5-19})$$

Where

$E_{EM}$ = electric energy per mass (kWh)

$c_i$ = initial concentration of contaminant C

$P$ = rated power of the system (kW)

$c_f$ = final concentration of contaminant C

$V$ = volume of fluid treated (L)

$F$ = fluid volumetric flow rate (m<sup>3</sup>/h)

$t$  = elapsed time (h)

$M$ = molar mass (g/mol) of contaminant C

### 5.3.2 Electric energy per order

Bolton *et al.* suggest the use of this figure when contaminant concentration is low and the AOP is electric energy driven. It corresponds to a first order kinetic behavior. Electric energy per order (EEO) is the electric energy in kilowatt-hours (kWh) needed to degrade a contaminant C by one order of magnitude in a unit volume of polluted water or air.

$$E_{EO} = \frac{P}{F \log\left(\frac{c_i}{c_f}\right)} \quad (\text{Eq. 5-20})$$

$$E_{EO} = \frac{Pt1000}{V \log\left(\frac{c_i}{c_f}\right)} \quad (\text{Eq. 5-21})$$

Where

$E_{EO}$ = electric energy per order (kWh)

$c_i$ = initial concentration of contaminant C

$P$ = rated power of the system (kW)

$c_f$ = final concentration of contaminant C

$V$ = volume of fluid treated (L)

$F$ = fluid volumetric flow rate (m<sup>3</sup>/h)

### 5.3.3 Collector area per mass

When solar driven systems handle large influent concentrations of a given pollutant, the collector area per mass ( $A_{CM}$ ) is suggested.  $A_{CM}$  is based on a zero order kinetic behavior. In other words it is the collector area required to bring about the degradation of a unit mass of a contaminant C in a polluted fluid in a time when the incident solar irradiance is  $1000 \text{ W/m}^2$ . Equations 5-22 and 5-23 describe  $A_{CM}$ :

$$A_{CM} = \frac{A\bar{E}_s t 1000}{E_s^o t_o M V (c_i - c_f)} \quad (\text{Eq. 5-22})$$

$$A_{CM} = \frac{A\bar{E}_s}{M F (c_i - c_f)} \quad (\text{Eq. 5-23})$$

Where

$A_{CM}$ = collector area per mass ( $\text{m}^2/\text{kg}$ )

$E_s$ = average solar irradiance ( $\text{W/m}^2$ )

$V$ = volume of fluid treated (L)

$t$  = elapsed time (h)

$t_o=1$  (h)

$M$ = molar mass (g/mol) of contaminant C

$c_i$ = initial concentration of contaminant C

$c_f$ = final concentration of contaminant C

$F$ = fluid volumetric flow rate ( $\text{m}^3/\text{h}$ )

$A$ = actual collector area ( $\text{m}^2$ )

$E_s^o=1000$  ( $\text{W/m}^2$ )

### 5.3.4 Collector area per order

This figure-of-merit is used in solar driven *AOPs* when the concentration of contaminant C is less than 100 mg/L. It describes a first order kinetic behavior. Collector area per order ( $A_{CO}$ ) stands for the collector area required to reduce the concentration of a contaminant C in a unit volume of polluted fluid by one order of magnitude in a time  $t_0$  (1 h) when the incident solar irradiance is 1000 W/m<sup>2</sup>.  $A_{CO}$  is described by equations 5-24 and 5-25.

$$A_{CO} = \frac{A\bar{E}_s t}{V \log\left(\frac{c_i}{c_f}\right)} \quad (\text{Eq. 5-24})$$

$$A_{CO} = \frac{A\bar{E}_s}{F \log\left(\frac{c_i}{c_f}\right)} \quad (\text{Eq. 5-25})$$

Where

$A_{CO}$  = collector area per order (m<sup>2</sup>/m<sup>3</sup>-order)

$E_s$  = average solar irradiance (W/m<sup>2</sup>)

$V$  = volume of fluid treated (L)

$t$  = elapsed time (h)

$c_i$  = initial concentration of contaminant C

$c_f$  = final concentration of contaminant C

$F$  = fluid volumetric flow rate (m<sup>3</sup>/h)

$A$  = actual collector area (m<sup>2</sup>)

Figures-of-merit proposed by the authors link kinetic reaction considerations with the energy received by the system and all are presented in the units of the largest economical cost. Therefore, the lower the result, the less energy must be supplied to the system and it will be more efficient.  $E_{EM}$ ,  $E_{EO}$ ,  $A_{CM}$  and  $A_{CO}$  are energy efficiency figures-of-merit; to fully evaluate the most cost-effective system other factors must also be considered.