CHAPTER 2

An overview of techniques used in analysis and treatment of aromatic sulphonates in aqueous environment
2.1 Introduction

The analytical studies of pollutants in aquatic environment are a very complex task. It includes the sample collection, pretreatment, extraction, enrichment, derivatization, separation and determination by advanced analytical techniques. The general scheme of analytical procedures for determination of organic pollutants is presented in Fig. 2.1. Chromatography in its different forms has become the leading analytical technique for separation of components from a mixture (Fig. 2.2).

![General scheme for determination of organic pollutants in water.](image)

CE: Capillary electrophoresis; GC: Gas chromatography; LC: Liquid chromatography; LLE: Liquid-liquid extraction; LPME: Liquid-phase micro extraction; MS: Mass spectrometry; SPE: Solid phase extraction; SPME: Solid phase microextraction.
It was first discovered by Tswett [1], a Russian botanist, who used to separate plant pigments. In 1952 A.J.P Martin and R.L.M. Synge were awarded the Nobel Prize in Chemistry for their invention of partition chromatography [2]. Even though a number of techniques have been developed for separation in liquid, gas and supercritical fluid phases, such as thin layer chromatography (TLC), liquid-chromatography (LC), gas chromatography (GC), supercritical fluid chromatography (SFC), capillary electrophoresis (CE) and capillary electro chromatography (CEC), the most common approaches for separation and determination of organic pollutants in water are gas chromatography (GC), high performance liquid chromatography (HPLC) and capillary electrophoresis (CE). General classification of chromatographic systems is shown in Fig. 2.2.

2.1.1 Gas chromatography (GC)

Since the separation by GC occurs in a gas phase, liquid samples have to be vaporized. This represents the main constraint of GC since the analytes have to be thermostable and sufficiently volatile. The strength of GC is its high efficiency and high separation capability. This technique is suitable for all kinds of volatile analytes, but not for non-volatile and thermally labile compounds. This technique is most suitable for the multiresidue analysis of pesticides in environmental matrices [3-5]. The polar compounds need to be derivatized prior to determination [6-8].
2.1.2 Liquid chromatography (LC)

LC has become a prominent tool for quantification of various substances in different matrices. LC is a separation process in which the sample mixture injected into a column and is distributed between two phases. One phase is the stationary phase immobilized on an inert surface in a column and the other a mobile solvent passing through the column. The detection of compounds has been carried out using different types of detectors viz., absorbance detectors (UV, PDA), fluorescence,
electrochemical, refractive index and mass spectrometric detectors (Fig. 2.3). Absorbance, fluorescence and mass spectrometric detectors have gained importance in the analysis of organic pollutants in water.

Fig. 2.3 Analytical LC/MS configuration.

### 2.1.3 Capillary electrophoresis

Capillary electrophoresis (CE) is related to the family of separation techniques that use narrow-bore fused-silica capillaries to separate a complex array of large and small molecules. High electric field strengths are used to separate molecules based on differences in charge, size and hydrophobicity. Sample introduction is accomplished by immersing the end of the capillary into a sample vial and applying pressure, vacuum or voltage. Depending on the types of capillaries and electrolytes used, CE can be segmented into several separation techniques viz., capillary zone
electrophoresis (CZE), micellar electrokinetic chromatography (MEKC), capillary gel electrophoresis (CGE), capillary electro-chromatography (CEC) and isotochophoresis (ITP). Although CE may be applied to different types of research, it has gained its reputation from the study of molecules that have traditionally been difficult to separate. In general, CE should be considered first when dealing with highly polar, charged analytes. Like HPLC, several types detectors viz., UV-Visible, fluorescence and mass spectrometric detectors are used in CE. Unfortunately CE suffers with low sensitivity and irreproducibility. Several workers have used CE to determine aromatic sulfonic acids [9] in water.

2.2 Absorbance detectors

Absorbance detectors measure the absorption at one or more wavelengths in the UV or visible light region. These are the most commonly used detectors since they are cheap, robust, easy to handle and sensitive for compounds with high molar absorptivity (ε). The detector response is a function of molar absorptivity, concentration of the compound and length of the cell. It is also affected by system parameters as: pH of the mobile phase, background noise, band broadening etc. Generally the absorbance (UV) detectors measure a single wavelength at a time. A photodiode-array (PDA) detector has the advantage of measuring absorption at several wavelengths simultaneously. It is also possible to obtain spectral information for each eluting peak in the LC-system. It can
provide information about peak purity and reveal if peaks in the chromatogram are related to the “parent” compound (e.g. degradation products and metabolites). Several workers have reported the use of UV and PDA detectors for analysis of aromatic sulfonic acids [10-12] in water.

### 2.2.1 Fluorescence detector

Many compounds have the ability to absorb UV-light and then re-emit light of a longer wavelength (less energy). If light is re-emitted with a short delay, the compound is fluorescent and if there is a somewhat longer delay it is phosphorescent. Some compounds have a strong natural (native) fluorescence while others have to be treated with reagents to form fluorescent derivatives. Fluorescence detectors are more sensitive than regular absorbance detectors for favorable compounds. Compounds with conjugated cyclic structures like polycyclic aromatic hydrocarbons (PAH) have a strong native fluorescence. Several workers have used this detector for determination of aromatic sulfonic acids [1,13] in water.

### 2.2.2 Mass spectrometric detectors

The mass spectrometer, in combination with a chromatographic inlet system, is probably the most powerful and useful tool available for analysis of environmental samples. Chromatography is an efficient separation technique, which uses a variety of sensitive and selective detectors to analyze a wide array of compounds. However, these detectors do not provide much information about the molecules being detected. In
chromatography, retention time is the major piece of information used to identify a compound. If two compounds have very close retention times, identification becomes very difficult. The mass spectrometer, however, provides information about the structure of the molecule. Liquid chromatography-mass spectrometry (LC-MS) has become an invaluable technique for trace analysis of polar compounds in aqueous samples of the environment and in water treatment. A typical LC/MS configuration is shown in Fig.2.3 LC-MS is of particular importance due to the impetus it has provided for research into the occurrence and fate of polar contaminants, and of their even more polar transformation products. Mass spectrometric detection and identification is most widely used in combination with sample preconcentration, chromatographic separation and atmospheric pressure ionization (API). The focus of this chapter is directed particularly toward instruments and method development with respect to their applications for detecting emerging contaminants. The current status and future perspectives of 1) mass analyzers, 2) ionization techniques to interface liquid chromatography (LC) with mass spectrometry (MS), 3) methods for preconcentration and separation with respect to their application for analysis of contaminants in water are discussed. Quadrupole and ion trap mass analyzers with electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) are generally useful techniques in routine analysis. Time-of-flight (TOF) mass spectrometers are of particular interest for accurate mass measurements
for identification of unknowns. For non-polar compounds, different ionization approaches have been described, such as atmospheric pressure photoionization (APPI), electrospray ionization (ESI). In sample preconcentration and separation, solid phase extraction (SPE) with different non-selective sorbent materials and HPLC on reversed-phase materials (RP-HPLC) plays the dominant role. In addition, various on-line and miniaturized approaches for sample extraction and sample introduction into the MS have been used. Ion chromatography (IC), size exclusion chromatography (SEC), and capillary electrophoresis (CE) are alternative separation techniques. Furthermore, the issues of compound identification, matrix effects on quantitation, development of mass spectral libraries and the topic of connecting analysis and toxicity bioassays were addressed.

In a mass spectrometer, a molecule is ionized, fragmented, and then the molecular mass of each fragment ion is determined. Each molecule forms a unique set of fragments, so the mass spectrum shows a pattern, which can be considered as a fingerprint of the molecule. The coupling of liquid chromatograph with mass spectrometry has been more challenging. Several types of interfaces such as fast-atom bombardment (FAB), matrix assisted laser desorption ionization (MALDI), thermospray (TSP), particle beam (PB) and direct liquid introduction (DLI) have been developed. The two major difficulties in combining LC and MS have been to accomplish ionization of nonvolatile and/or thermally labile analytes and to solve the
flow rate incompatibility. These two obstacles were successfully solved by
the introduction of two atmospheric pressure ionization techniques viz.,
electrospray ionization (ESI) and atmospheric pressure chemical ionization
(APCI). The soft ionization feature of electrospray ionization allows
formation of ions from highly polar, thermolabile and nonvolatile
compounds. Several workers used ESI for analysis of aromatic sulfonic
acids [14-21] in water whereas very few reports were available for use of
APCI for the analysis of aromatic sulfonic acids in water [22].

2.3 Treatment of wastewater contaminated with aromatic
sulphonates

The control of water pollution is of increasing importance in recent
years. Stringent government regulations force the chemical industries to
treat their waste effluent to an increasingly high standard. Unlike other
industries, the effluents generated from chemical processing units are
characteristically different with respect to quality and quantity. The
variable nature of wastewater generated from these units can be
attributed due to the process variation and consumption of large quantity
of organic and inorganic materials. Treatment of wastewater generated
from chemical processes is considered to be complex due to the presence
of recalcitrant organic compounds present in the wastewater like solvents
and inorganic salts.
The release of dyes into the environment constitutes only a small proportion of water pollution, but dyes are visible in small quantities due to their brilliance. Many studies were conducted to treat the presence of aromatic sulphonlic acids in wastewaters. Initially color was considered as one of the most undesirable characteristics. Oliver J. Hao, et.al proposed that a combination of chemical-biological, biological-chemical, chemical-physical, chemical-chemical, etc. often used for decolorization. The formation of intermediates during the decolorization process may be more toxic than the parent compounds. Thus, the extent of the mineralization in waste decolorization should be evaluated [23].

The wastewater from chemical industries is generally treated to remove the contaminants so that it meets the acceptable quality standards. The quality standards usually depend upon whether the water will be reused or discharged into a receiving stream. The available wastewater treatment processes could be broadly classified as physical, chemical or biological. These processes consist of a series of unit operations and applied in different combinations and sequences depending upon the prevailing situations of influent concentration, composition, condition and specifications of the effluent. For instance, the combination of treatment procedures used for treatment of effluents of a textile industry is shown in Fig. 2.4. Some of the physical, chemical, biological processes used are discussed below.
2.3.1 Air stripping

Air stripping involves the transfer of volatile organics from liquid phase to the air by increasing the air/water contact area. Typical aeration methods include packed towers, diffusers, trays, and spray aeration. It is
an established and more widely understood technology than chemical oxidation. It can be accurately designed from theory and experience without the need for design tests. If air emissions are not regulated, air stripping is by far the simplest and cheapest solution for removal of volatile compounds from water. It is used as pretreatment to remove high solvent content present in wastewater. But this technique is not suitable for the removal of highly polar and nonvolatile compounds viz., aromatic sulfonic acids from water.

### 2.3.2 Adsorption

Adsorption is a physical treatment where the pollutants physically adsorb onto the surface of the adsorbent via weak electrostatic forces of attraction. Activated carbon is the most commonly used adsorbent for removal of organic compounds from groundwater and industrial waste streams. Although carbon adsorption is a well-developed technology utilized widely in drinking water systems as well as for pollution control, it has drawbacks, which include:

i) The high cost of activated carbon,

ii) Activated carbon is usually loaded into and out of the adsorbers using water-carbon slurries, which increases system complexity and cost, and
iii) The spent activated carbon typically has to be transported to a different site to be either regenerated or disposed off, which increases operating costs.

Due to these drawbacks, there exists scope for replacement of activated carbon with innovative, yet cost effective natural adsorbents. Further several workers have investigated the use of natural adsorbents viz., kenaf, peat mass, hay and peanut hulls. The use of clay materials, mesoporous silica materials and cellulose fibers was also studied as an alternative to activated carbon. The adsorption of aromatic sulfonic acids was studied by several workers [24,25]. But the process is non-destructive and has disposal problems of removed sludge.

2.3.3 Wet oxidation

In the wet oxidation processes, organic and inorganic compounds are oxidized in aqueous phase, with oxygen or air, at high pressures and temperatures. The temperature depends on the nature of the compounds to degrade. However it varies between 150 and 350°C. Pressure goes from 20 to 200 bars. The mechanism of wet oxidation has been extensively studied and seems to take place by means of a free radical process. Among the compounds that have been catalogued as readily oxidizable by means of wet oxidation are aliphatic chlorides and aromatics, which do not contain halogenated functional groups, such as phenols or anilines. Compounds containing halogen and nitro functional groups have been
found to be difficult to degrade by this technique. Very few reports \[26,9\] are available for treatment of aromatic sulfonic acids by means of wet oxidation.

### 2.3.4 Reverse osmosis

Reverse osmosis is a process of pushing a solution through a filter that traps the solute on one side and allows the pure solvent to be obtained from the other side. More formally, it is the process of forcing a solvent from a region of high solute concentration through a membrane to a region of low solute concentration by applying a pressure in excess of the osmotic pressure. This is the reverse of the normal osmosis process, which is the natural movement of solvent from an area of low solute concentration, through a membrane, to an area of high solute concentration when no external pressure is applied. The membrane here is semipermeable, which allows the passage of solvent but not of solute. This process is best known for its use in desalination (removing the salt from sea water to get fresh water) and has been used since 1970s. Even though it is used for the removal of salts and heavy metals present in aqueous samples and for the concentration of fruit juices to retain the profile of aroma, several workers have reported the removal of organic contaminants from wastewaters and industrial effluents [27-29]. But no reports are available for aromatic sulfonic acids. It is non-destructive and has disposal problem of removed sludge.
2.3.5 Electrochemical oxidation

The use of electrochemical oxidation for destruction of organic compounds in water was tried on bench and pilot plant scale [30,31]. It was not used commercially because of its high operating costs. One of the main advantages of the electrochemical processes is that electrons are given or consumed within the electrodes, supplying a clean reactant, which does not increase the number of chemical molecules involved in the process. Nevertheless, they present some disadvantages viz., i) the electrochemical treatment is expensive when compared with other processes and the mechanism is rather complex and ii) the necessity of the effluent to be conductor, therefore in case that the stream to be treated does not present a good conductivity a salt should be added.

The mechanism of the electrochemical processes involves three stages viz., i) electrocoagulation,

ii) electroflotation and

iii) electrooxidation.

The anodic oxidation is generally considered to be a direct technique. It involves transfer of an electron from the organic molecule to the electrode, thus generating a cationic radical. In the direct way, the fate of the cationic radical, pH and the nature of the electrodes influence in a decisive manner on the formed products.

\[
\text{RH} \xrightarrow{-e-} \text{RH}^+ \quad \text{(Eq. 1)}
\]
Many articles were published describing the application of electrochemical processes in industrial wastewater treatment. But no reports were found on the electrochemical oxidation of aromatic sulfonic acids.

2.3.6 Biological detoxification

Biological treatment is preferred more for degradation of toxic organic substances for the following reasons:

- Economic over other methods.
- Diversity of degradation.
- Robust and have a large capacity for degrading toxic and hazardous materials.

2.4 Biodegradation

Biodegradation is a breakdown of organic contaminants by microorganisms into smaller compounds. The microorganisms transform the contaminants through metabolic or enzymatic processes. Biodegradation processes vary greatly, but frequently the final product of the degradation is carbon dioxide or methane. Biodegradation is a key process in the natural attenuation of contaminants at the sites of
hazardous waste. Biodegradation or transformation of organic compounds involves either of the processes of aerobic or anaerobic situation. In some cases it may need both the conditions to detoxify some of the xenobiotic compounds.

2.4.1 Aerobic degradation

In a conventional aerobic system, the substrate is used as a source of carbon and energy. It serves as an electron donor resulting in bacterial growth. The extent of degradation is correlated with the rate of $O_2$ consumption, and also previous acclimatization of the organism in the same substrate. Two enzymes primarily involved in the process are di- and mono-oxygenases. The later enzymes can act on both aromatic and aliphatic compounds, while the former, only on aromatic compounds. Another class of enzymes involved in aerobic condition is peroxidases, which are known for their ability to degrade lignin. Several workers have used this method for degradation of aromatic sulfonic acids [32-39].

2.4.2 Anaerobic degradation

Anaerobic process is of widespread occurrence and relies on the metabolic versatility of mixed microbial populations present in soils or sediments when oxygen supply is limited. Growth yield of anaerobic bacteria is extremely low due to low energy. It has drawn attention these years due to the possibility of decomposition of extremely recalcitrant
xenobiotics. Though the anaerobic process is slow, needs long retention time and produces \( \text{H}_2\text{S} \) gas, it is more advantageous than the aerobic due to its non-dependence of oxygen supply. It thus saves the cost of energy for transfer of oxygen. Few reports were available for degradation of aromatic sulfonic acids using this method [40,41].

2.4.3 Sequential degradation

In many cases, both anaerobic and aerobic processes are combined. This helps in reduction of toxicity and mineralization of compounds, which are otherwise recalcitrant. For example, many of the azo dyes initially form aromatic amines in anaerobic conditions, which are later converted into \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) in aerobic conditions. Several sulfonated azo dyes were treated using this method [42-45].

2.4.4 Cometabolism

Some of the pollutants can be degraded by microorganisms only in association with other utilizable substrates. Metabolism that cannot by itself support cell growth but support growth in the presence of another substance (co-substrate) is called cometabolism or co-oxidation. It has recently emerged as an important technique for treatment of many xenobiotic compounds. However, the presence of non-growth substrate can inhibit the metabolism of the natural growth substrate, because of its toxicity or recalcitrance, thereby decreasing cell growth and retarding biodegradation. Such cometabolism can be exploited, for example, by
purification of industrial effluents that contain degradation-resistant synthetics together with domestic sewage water in a common wastewater treatment plant. A number of organic compounds have been treated using cometabolism, but no reports were found for aromatic sulfonic acids.

### 2.5 Biosorption

Biosorption can be defined as sequestering of organic and inorganic species including metals, dyes and odor causing substances using live or dead biomass or their derivatives. This biomass may be bacteria, fungi, algae, sludge from biological wastewater treatment plants, by-products from fermentation industries or seaweeds. In this process, adsorbents are biological materials, and the removal mechanism is mainly sorption. Biosorption, if compared with other technologies such as precipitation, ion exchange, reverse-osmosis and adsorption, gives comparable performance at a very low cost. Apart from cost effectiveness and competitive performance, other advantages are possible regeneration at low cost, availability of known process equipment, sludge free operation and recovery of the sorbate.

The biosorption capacity of a biomass depends on several factors. It includes the type of biomass (species, age), sorbates, presence of other competing ions and method of biomass preparation (culture condition for live biomass), along with several physico-chemical factors (temperature, pH, ionic concentration). Over the past few decades, a number of
biological materials have been studied for the sorption of different types of pollutants. A wide variety of microorganisms, including bacteria, algae and fungi, are capable of sorbing a number of pollutants. Among the commonly available sorbents, macro fungus possesses the characteristics of an ideal biosorbent. It is easily available, especially in locations with hot and humid climates such as India. A macro fungus-based biosorbent is chemically stable in most alkaline and acidic conditions. It also possesses good mechanical properties against abrasion. Several sulfonated azo dyes were treated using biosorption [46-48].

2.6 Chemical oxidation

Oxidation, by definition, is a process by which electrons are transferred from one substance to another. This leads to a potential expressed in volts referred to a normalized hydrogen electrode. From this, oxidation potentials of the different compounds are obtained. Table 2.1 shows the oxidation potentials of the most commonly used oxidizers.

Chemical oxidation leads to the formation of biodegradable compounds and not those of CO₂ and H₂O. It is an appropriate technique for small loads (small volumes of sample) of pollutants. This would otherwise become an expensive technique, because of its large oxidizer consumption. In general, chemical oxidation shows good prospects for use in the elimination of non-biodegradable compounds in the following cases:
(a) For treatment of high concentrations of the compounds to be eliminated, without the interference of others.

(b) As a pretreatment of effluents, to reduce toxicity by avoiding problems of inhibition in the biomass.

(c) As a final treatment for adjustment of the effluent for the desired discharging conditions.

The chemical oxidation processes can be divided into two classes such as

i) Classical chemical treatments

ii) Advanced oxidation processes (AOPs)

Table 2.1 Oxidation potentials of selected oxidizing agents

<table>
<thead>
<tr>
<th>Oxidation agent</th>
<th>Oxidation potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorine</td>
<td>3.03</td>
</tr>
<tr>
<td>Hydroxyl radical</td>
<td>2.80</td>
</tr>
<tr>
<td>Atomic oxygen</td>
<td>2.42</td>
</tr>
<tr>
<td>Ozone</td>
<td>2.07</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>1.77</td>
</tr>
<tr>
<td>Permanganate</td>
<td>1.67</td>
</tr>
<tr>
<td>Hypobromous acid</td>
<td>1.59</td>
</tr>
<tr>
<td>Chlorine dioxide</td>
<td>1.50</td>
</tr>
<tr>
<td>Hypochlorous acid</td>
<td>1.49</td>
</tr>
<tr>
<td>Hypoiodous acid</td>
<td>1.45</td>
</tr>
<tr>
<td>Chlorine</td>
<td>1.36</td>
</tr>
<tr>
<td>Bromide</td>
<td>1.09</td>
</tr>
<tr>
<td>Iodine</td>
<td>0.54</td>
</tr>
</tbody>
</table>
2.6.1 Classical chemical treatments

Classical chemical treatments are generally based on the addition of an oxidizing agent to the water containing the contaminants. The most widely used chemical oxidants are as follows:

**Chlorine:** This is a good chemical oxidizer for water purification. It destroys microorganisms. It is a strong and cheap oxidant, very simple to feed into the system. Its main disadvantages are its little selectivity that high amounts of chlorine are required and it usually produces carcinogenic organochlorine by-products.

**Potassium permanganate:** It has been extensively used in the treatment of water for decades. It can be introduced into the system as a solid or as a solution prepared on site. It is a strong but expensive oxidant, which works properly in a wide pH range. One of the disadvantages of the use of potassium permanganate is the formation of manganese dioxide, which has to be eliminated afterward by clarification or filtration, both of which mean an extra cost.

**Oxygen:** The reaction of organic compounds with oxygen does not take place at normal temperatures and pressures. Needed values of temperature and pressure are high to increase the oxidizing character of the oxygen in the reaction medium and to assure the liquid state of the effluent. It is a mild oxidant that requires large investments in installations. However, its low operating costs make the process attractive.
**Hydrogen peroxide:** It is a multipurpose oxidant for many systems. It can be applied directly or with a catalyst. The catalyst normally used is ferrous sulphate (the so-called Fenton process). Other iron salts can be used as well. Other metals can also be used as catalyst, for example, Al\(^{3+}\), Cu\(^{2+}\). Its basic advantages are i) it is one of the cheapest oxidizers that is normally used in residual waters, ii) it has high oxidizing power, iii) it is easy to handle, iv) it is water-soluble and v) it does not produce toxins or colored byproducts. It can also been used in presence of ultraviolet radiation and the oxidation is based on the generation of hydroxyl radicals that was considered to be an advanced oxidation process.

**Ozone:** Among the most common oxidizing agents, it is only surpassed in oxidizing power by fluorine and hydroxyl radicals (Table 2.1). It offers the advantage of, as hydrogen peroxide and oxygen, not introducing “strange ions” in to the medium. Ozone is effective in many applications, like removal of color, disinfection, smell, taste and organic compounds. In standard conditions of temperature and pressure it has a low solubility in water and is unstable. It has an average life of a few minutes. Therefore, to have the necessary quantity of ozone in the reaction medium a greater quantity has to be used. The major disadvantage of ozone is that it has to be produced *in situ* and needs installation of an ozone production system in the place of use. Therefore, the cost of this oxidizer is extremely high, and it must bear this in mind when deciding the most appropriate oxidizer for a given system.
Ozonation is used in many drinking water plants as a tertiary treatment and also for oxidation of organic pollutants of industrial (paper industry) or agriculture (water polluted by pesticides) effluents. A lot of research was carried out to investigate the kinetics of the ozonation reaction of various organic and inorganic compounds. Several workers have studied the degradation of naphthalene sulfonic acids and sulfonated azodyes using ozone [49-51]. This process was able to increase biodegradability, but not complete mineralization.

2.6.2 Advanced oxidation processes

Advanced oxidation processes (AOPs) are attractive alternatives for treatment of contaminated water containing hardly-biodegradable anthropogenic substances as well as purification and disinfection of drinking waters. AOPs are useful complements to well established techniques like flocculation, precipitation, adsorption on activated carbon, air stripping, reverse osmosis, combustion and biological oxidation. These AOPs include O₃/UV, H₂O₂/UV, O₃/H₂O₂/UV, Fe²⁺/H₂O₂, Fe²⁺/H₂O₂/UV and TiO₂/UV processes.

2.6.2.1 H₂O₂/UV process

The H₂O₂/UV system involves the formation of ‘OH radicals by hydrogen peroxide photolysis and subsequent propagation reactions. The
most commonly accepted mechanism for photolysis of H₂O₂ is the cleavage of the molecule into hydroxyl radicals:

\[
\text{hv} \quad \text{H}_2\text{O}_2 \rightarrow \quad 2 \cdot \text{OH} \quad \lambda \leq 300 \text{ nm} \quad (\text{Eq. 4})
\]

It provides a cheap and sure source of radicals, eliminating the problem of handling of ozone. The major drawback of this process is that it needs UV radiation < 300 nm, which prevents the use of solar radiation.

The effectiveness of the H₂O₂/UV system in treatment of sulfonated azodyes was studied [52,53]. However, in case of aromatic sulfonic acids no reports were found in the literature.

### 2.6.2.2 O₃/UV process

Photolysis of ozone dissolved in water leads to the production of hydrogen peroxide (Eq.5) and the subsequent formation of \( \cdot \text{OH} \) (Eq.4), which oxidizes the organic compounds. Direct oxidation of the pollutants by O₃ is also involved. The O₃/UV process is considered to be advanced water treatment for effective oxidation and destruction of toxic and refractory organics, bacteria, and viruses in water. However, it has the same problems as hydrogen peroxide process for use of solar energy since O₃ does not absorb light at \( \lambda > 300 \text{ nm} \).

\[
\text{hv} \quad \text{O}_3 + \text{H}_2\text{O} \rightarrow \quad \text{O}_2 + \text{H}_2\text{O}_2 \quad (\text{Eq. 5})
\]

Very few reports were available on degradation of aromatic sulfonic acids and sulfonated azo dyes using this method [54].
2.6.2.3 \textbf{O}_3 /\text{H}_2\text{O}_2/\text{UV process}

This process is a combination of the binary systems \text{UV}/\text{O}_3 and \text{O}_3/\text{H}_2\text{O}_2. The addition of \text{H}_2\text{O}_2 to the \text{UV}/\text{O}_3 process accelerates decomposition of ozone resulting in increased rate of ‘\text{OH} radicals generation. This is a very powerful method that allows a considerable reduction of TOC.

2.6.2.4 \textbf{Fenton and photo-Fenton reactions}

The Fenton reaction was discovered by H.J. Fenton in 1894 [55]. Forty years later the Haber-Weiss (1934) mechanism was postulated, which revealed that the effective oxidative agent in the Fenton reaction was the hydroxyl radical. The Fenton reaction can be outlined as follows:

\begin{equation}
\text{M}^{n+} + \text{H}_2\text{O}_2 \rightarrow \text{M}^{(n+1)+} + \cdot\text{OH} + \cdot\text{OH}
\end{equation}

where \text{M} is a transition metal as \text{Fe} or \text{Cu}.

In absence of light and complexing ligands other than water, the most accepted mechanism of \text{H}_2\text{O}_2 decomposition in homogeneous aqueous solution, involves the formation of hydroxyperoxyl (\text{HO}_2^+/\text{O}_2^-) and hydroxyl radicals (‘\text{OH}).

The ‘\text{OH} radical, once in solution attacks almost every organic compound. The metal regeneration can follow different paths. For \text{Fe}^{2+}, the most accepted scheme is described in Equations 7 to 13.

\begin{equation}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \cdot\text{OH}
\end{equation}

\begin{equation}
\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{HO}_2^- + \text{H}^+
\end{equation}
\[ \text{Fe}^{2+} + \cdot \text{OH} \rightarrow \text{Fe}^{3+} + \cdot \text{OH} \quad \text{(Eq. 9)} \]

\[ \cdot \text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^* + \text{H}_2\text{O} \quad \text{(Eq. 10)} \]

\[ \text{Fe}^{3+} + \text{HO}_2^* \rightarrow \text{Fe}^{2+} + \text{H}^+ \text{+ O}_2 \quad \text{(Eq. 11)} \]

\[ \text{Fe}^{3+} + \text{O}_2^* \rightarrow \text{Fe}^{2+} + \text{O}_2 \quad \text{(Eq. 12)} \]

\[ \text{Fe}^{2+} + \text{HO}_2^* \rightarrow \text{Fe}^{3+} + \text{HO}_2^- \quad \text{(Eq. 13)} \]

Fenton reaction rates are strongly increased by irradiation with UV/visible light. During the reaction, \( \text{Fe}^{3+} \) ions are accumulated in the system and after \( \text{Fe}^{2+} \) are consumed, the reaction practically stops. Photochemical regeneration (Eq. 14) of ferrous ions (\( \text{Fe}^{2+} \)) by photoreduction of ferric ions (\( \text{Fe}^{3+} \)) is then proposed. The generated ferrous ion reacts with \( \text{H}_2\text{O}_2 \) generating a \( \cdot \text{OH} \) radical and ferric ion, and the cycle continues.

\[ \text{Fe}^{3+} + \text{H}_2\text{O} + \text{hv} \rightarrow \text{Fe}^{2+} + \cdot \text{OH} \quad \text{(Eq. 14)} \]

Fenton and photo-Fenton reactions depend not only on \( \text{H}_2\text{O}_2 \) concentration and iron added, but also on the operating pH value. Several workers have studied the use of Fenton and photo-Fenton process for degradation of aromatic sulfonic acids and sulfonated azo dyes [10, 11, 56-66].

### 2.6.2.5 \textbf{TiO}_2/UV process (Heterogeneous photocatalytic degradation)

Heterogeneous photocatalysis involves irradiation of a catalyst, usually a semiconductor, which is photoexcited to form electron-donor
(reducing) and electron-acceptor (oxidizing) sites, providing a great scope as redox reagents. The process is heterogeneous because there are two active solid and liquid phases.

The molecular orbitals of semiconductors have a band structure. The bands of interest in photocatalysis are the occupied valence band (VB) and the unoccupied conductance band (CB), separated by an energy distance referred to as the band gap ($E_{bg}$). When the semiconductor is illuminated with light ($h\nu$) of higher energy than that of the band gap, an electron is promoted from the VB to the CB leaving a positive hole in the valence band. After separation, the electron ($e^-$) and hole ($h^+$) pair may recombine generating heat or involve in electron transfer reactions with other species in solution. The oxidation or reduction of electron-donor (D) or electron-acceptor (A) species is shown in Fig. 2.5.

For oxidation reactions to occur, the VB must have a higher oxidation potential than the material under consideration. The redox potential of the VB and CB for different semiconductors varies between $+4.0$ and $-1.5$ volts versus Normal Hydrogen Electrode (NHE) respectively. Therefore, by selecting suitable semiconductor photocatalysts, a wide range of species can be treated via these processes. Several oxidative semiconductors such as TiO$_2$, ZnO, ZnS, SnO$_2$, WO$_3$, CdS, CdSe, GaAs, GaP and bimetallic catalysts such as TiO$_2$/SiO$_2$, V$_2$O$_5$/TiO$_2$, Bi$_2$WO$_6$, Pd-Pt/Al$_2$O$_3$ and BaO-LiO$_2$-TiO$_2$ have been evaluated as heterogeneous photo catalysts.
Fig. 2.5 Illumination of a semiconductor. Promotion of an electron from the VB to the CB and fate of electrons and holes generated in presence of electron acceptors (A) and donors (D).

Table 2.2 lists some of the selected semiconductor materials, which have been used for photo catalytic reactions, together with the VB and CB potentials and the band gap energy and wavelength of UV radiation required to activate the catalyst. To produce this gap, the radiation must be of a $\lambda$ equal or lower than the calculated by the Planck's equation (Eq.15).

$$\lambda = \frac{hc}{E_{bg}} \quad \text{(Eq. 15)}$$

Where $E_{bg}$ is the semiconductor band-gap energy, $h$ is the Planck's constant and $c$ is the speed of light.
Among the listed semiconductors, TiO$_2$ has proven to be the most suitable for widespread environmental applications. TiO$_2$ is biologically and chemically inert. It is stable to photochemical corrosion, and inexpensive. Furthermore, TiO$_2$ is of special interest since it can use natural (solar) UV radiation. Although ZnO seems to be a suitable alternative to TiO$_2$, it dissolves in acidic solutions and therefore cannot be used for technical applications [33]. Other semiconductor particles (e.g., CdS or GaP) absorb larger fractions of the solar spectrum than TiO$_2$ and can form chemically activated surface-bond intermediates. However, such catalysts degrade during the repeated catalytic cycles usually involved in heterogeneous photocatalysis.

Table 2.2 Band positions of some common semiconductor photocatalysts in aqueous solution at pH=1

<table>
<thead>
<tr>
<th>Semi-Conductor</th>
<th>Valence band (eV vs NHE)</th>
<th>Conductance band (eV)</th>
<th>Band gap (eV vs NHE)</th>
<th>Band wave-length (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>+3.1</td>
<td>-0.1</td>
<td>3.2</td>
<td>387</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>+4.2</td>
<td>+0.3</td>
<td>3.9</td>
<td>318</td>
</tr>
<tr>
<td>ZnO</td>
<td>+3.0</td>
<td>-0.2</td>
<td>3.2</td>
<td>387</td>
</tr>
<tr>
<td>ZnS</td>
<td>+1.4</td>
<td>-2.3</td>
<td>3.7</td>
<td>335</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>+3.0</td>
<td>+0.2</td>
<td>2.8</td>
<td>443</td>
</tr>
</tbody>
</table>
The commercially available TiO$_2$ Degussa P25 (anatase: rutile ratio, 80:20) has become the standard for photoreactivity in environmental applications [58,59]. Other types such as Hombikat and Millennium etc., [60] and surface modified TiO$_2$ were also used in heterogeneous photocatalysis [35]. The P25 TiO$_2$ powder has a surface area of 50 m$^2$ g$^{-1}$ and an average particle diameter of 21 nm. It is important to note that 90% of the material does not exist as isolated particles, but rather as irreducible complex primary aggregates, typically of approximately 0.1 μm in diameter. The VB and CB positions for Degussa P25 have been calculated as +2.9 and -0.3 V, respectively.

### 2.6.2.6 Mechanism of the TiO$_2$ - photocatalysed degradation

To date, there is enough evidence supporting the idea that hydroxyl radical ($\bullet$OH) is the main oxidizing species responsible for photo-oxidation of the majority of the organic compounds. The first event, after absorption of near ultraviolet radiation at $\lambda$<380 nm, is the generation of electron/hole pairs (Eq.16) separated between the CB and VB.

\[
\text{TiO}_2 + h\nu \rightarrow \text{TiO}_2 (e^- + h^+) \quad (\text{Eq.16})
\]
Some of the many events, which take place after the UV light absorption by TiO₂ particles are summarized in equations 17 to 24. Three oxidation reactions have been experimentally observed: i) electron transfer from RX (Eq. 17), ii) H₂O (Eq. 18), and iii) -OH (Eq. 19) adsorbed on the catalyst surface. Reactions 18 and 19 appear to be of great importance in oxidative degradation processes, most probably due to the high concentration of -OH and H₂O adsorbed on the TiO₂ surface.

\[
\text{TiO}_2 (h^+) + RX \rightarrow \text{TiO}_2 + R^+ + H^+ \quad \text{(Eq. 17)}
\]

\[
\text{TiO}_2 (h^+) + \text{H}_2\text{O}_{ad} \rightarrow \text{TiO}_2 + \cdot\text{OH}_{ad} + H^+ \quad \text{(Eq. 18)}
\]

\[
\text{TiO}_2 (h^+) + \cdot\text{OH}_{ad} \rightarrow \text{TiO}_2 + \cdot\text{OH}_{ad} \quad \text{(Eq. 19)}
\]

Molecular oxygen, which must be present in all oxidative degradation processes, is the acceptor species in an electron-transfer reaction with the photocatalyst CB (Eq. 20). Superoxide anion and its protonated form subsequently combine to yield hydrogen peroxide. (Eqs 20-23).

\[
\text{TiO}_2 (e^-) + O_2 \rightarrow \text{TiO}_2 + O_2^- \quad \text{(Eq. 20)}
\]

\[
O_2^- + H^+ \rightarrow \cdot\text{HO}_2^- \quad \text{(Eq. 21)}
\]

\[
O_2^- + \cdot\text{HO}_2^- \rightarrow \cdot\text{OH} + O_2 + \text{H}_2\text{O}_2 \quad \text{(Eq. 22)}
\]

\[
2\cdot\text{HO}_2^- \rightarrow \text{O}_2 + \text{H}_2\text{O}_2 \quad \text{(Eq. 23)}
\]

Hydrogen peroxide addition considerably enhances the photo degradation rate, most probably via reaction 24.

\[
\text{TiO}_2 (e^-) + \text{H}_2\text{O}_2 \rightarrow \text{TiO}_2 + \cdot\text{OH} + \text{OH}^- \quad \text{(Eq. 24)}
\]

Organic pollutants adsorbed on TiO₂ particles will then be oxidized by ‘OH radicals. Different heterogeneous catalysts viz., TiO₂, ZnO and
TiO$_2$/WO$_3$ were evaluated for degradation of aromatic sulfonic acids and sulfonated dyes [58,60,62,63].

### 2.6.2.7 AOPs combined with biological treatments

Biological treatment of wastewater, groundwater, and aqueous hazardous wastes is often the most economical alternative when compared with other treatment options. The ability of a compound to undergo biological degradation is dependent on a variety of factors, such as concentration, chemical structure and substituents of the target compound. The pH or the presence of inhibitory compounds can also affect the biological degradation. Although many organic molecules are readily degraded, many other synthetic and naturally occurring organic molecules are biorecalcitrant.

Several chemical processes, which use oxidizing agents such as ozone, hydrogen peroxide, etc. have been carried out to mineralize many synthetic organic chemicals. However, costs associated with chemical oxidation alone can often be prohibitive for wastewater treatment. A potentially viable solution is the integration of chemical and biological treatment processes as an economical means for treating biorecalcitrant organic chemicals in wastewater. The chemical process would be used as a pre-treatment in order to increase the biodegradability of wastewaters. The oxidation of organic compounds in water with AOPs usually produces oxygenated organic products and low molecular weight acids that are
more biodegradable. This feature is economically interesting, as investment and operating costs are much lower for a biological process than a chemical one: investments costs for biological processes range from 5 to 20 times less than chemical ones such as ozone or hydrogen peroxide, while treatment costs range from 3 to 10 times less [11,65].

During the last decade, many studies focused on the use of advanced oxidation processes as a pre-treatment step. In this sense, the first coupled flow system was developed by Pulgarin et al. [66]. Few reports were available in literature for degradation of aromatic sulfonic acids using this technique [67-70].
2.7 References


2. M. S. Tswett, presented at a meeting of the Biological Section of the Warsaw Society of Natural Sciences (1903).


23. Oliver J. Hao a Hyunook Kim a; Pen-Chi Chiang a


