Development of catalytic microreactors by plasma processes: application to wastewater treatment
Da Silva, B.T.
Chapter 2: Materials and methods

1. Introduction

The studies contained in this thesis were carried out in 2 segments: first, an investigation on the microfluidics materials suitable for the deposition of a support layer with a low pressure plasma process was performed using a home-made device. The second concerns the deposition of a catalyst coating by plasma process and the quantification of the catalytic activity using an advanced oxidation process.

Therefore, the plasma process used for the deposition of the silica-like layer and the catalyst as well as the catalytic ozonation process will be described here. The materials and analytical techniques used for the surface characterizations or for the analyses of the collected liquid samples are presented.

2. Microfluidic materials

Polymer-based microfluidic materials were investigated as flat substrates in order to assess the stability of the catalytic coating in the MO-PECVD process.

Flat substrates of Polydimethylsiloxane (PDMS) were prepared by pouring the monomer (Sylgard, Dow Corning) and hardener (respectively in ratio 9:1) in a 40 x 12 mm petri box. The curing was performed in an oven heated at 70°C for two hours. The PDMS samples were cut into square shapes of 2 x 2 cm.

Cyclic olefin copolymer (COC) films (Topas grade 6013, Tg = 130°C, 254 μm thickness) were purchased from Topas Advanced Polymers, Extrusion Lab (USA). Polymer sheets of 20 cm x 20 mm x 350 μm dimensions were obtained at 290°C from the COC pellets. The sheets were cut into 2 x 2 cm.

Norland Optical Adhesive (NOA) substrates were obtained by pressing a drop of NOA 81 between a flat PDMS stamp and a microscope glass slide. The resin was then UV-cured under 7 seconds of exposure with a 365 nm UV light (Hamamatsu LC8, lamp power of 10 mW/cm²). After reticulation, the NOA covered glass slide was cut into 2 x 2 cm and cleaned with isopropanol.
THV substrates (Dyneon) grade 500 were graciously provided by the Laboratoire des Macromolécules et Microsystèmes en Biologie et Médecine. A blank bare THV wafer of 5 mm thick was cut into 10 mm x 10 mm square shapes. Polished stainless steel 316L grade plates were purchased from Goodfellow (France). These samples of 15 mm x 15 mm and 1 mm thick were used as substrates for ellipsometry experiments. All substrates were cleaned by immersion in isopropanol or/and acetone solutions followed by a high-pressure, high-purity nitrogen gas drying step.

3. **Metal-Organic Plasma Enhanced Chemical Vapour Deposition Process**

3.1 **Description of the reactor**

The process used for the elaboration of the catalyst coatings is a home-made low pressure low temperature PECVD process. As shown in Figure 9, the reactor consists in a Pyrex tube of 60 cm of length and 46 mm of internal diameter. The reactor is equipped with a spray nozzle of 5 mm of diameter in order to focus the deposition on the substrate holder. Connected to a matching box, a 13.56 MHz radiofrequency generator is used to generate the plasma in the reactor via external parallel capacitive electrodes placed on the tube. Mass flow meters linked to a controller enable to vary the incoming gas flow. Vacuum is achieved by the use of a rotary vane pump and the pressure is read by means of a Pirani gauge placed at the end of the reactor. Regarding the organo-metallic precursor, it is placed in a flask above the reactor and introduced in droplets by the use of a nebulizer. The nebulizer is separated from the reactor by an electro-valve on which the opening and closing times can be adjusted. By over pressurization, the created droplets are brought in the gas phase via an introduction line which is heated above the boiling temperature of the precursor in order to avoid its condensation.
3.2 General procedure for the silica-like deposition

In order to clean off the surface of the samples from eventual adsorbed atmospheric contaminants, the samples are first exposed to a 200 W argon (150 sccm) and oxygen (150 sccm) plasma treatment during 10 min with a total pressure of 1.4 mbar. After this pre-treatment step, a gas mixture composed of oxygen (300 sccm) and hexamethyldisiloxane (60 sccm) is introduced in the reactor. The organo-silicon vapor is supplied to the reactor chamber from liquid HMDSO (Merk, 98.5%) contained in a cylindrical flask, via a stainless steel line heated at 70°C. A manual valve is used for fine control of the flow. The plasma power and deposition time are respectively of 150 W and 4 mn with a total pressure of 1.7 mbar.
3.3 General procedure for the catalyst deposition

After the deposition of the silica-like layer, a gas mixture composed of oxygen (300 sccm) and argon (300 sccm) is introduced in the reactor along with the organo-metallic precursor.

For the deposition of the cobalt oxide catalyst, 1g of cobalt carbonyl Co₂(CO)₈ (Strem Chemicals, France) dissolved in 20 mL of hexene is introduced in the flask. Dicobalt octacarbonyl is a metal organic compound solid under standard conditions which decomposes above 52 °C. The precursor reacts readily with hexene under formation of gas bubbles and a color change to deep violet occurs.

For the deposition of the iron oxide catalyst, 30 mL of iron pentacarbonyl Fe(CO)₅ (Sigma-Aldrich, France) are introduced in the flask. The introduction line is heated at 70°C and the electro-valve is set at 0.9 seconds for the opening time and closes during 4 seconds. The plasma power and deposition time are respectively of 200 W and 12 mn for a total pressure of 2 mbar. Activation of the catalyst is achieved using argon plasma (300 sccm) at a power of 150 W during 30 mn.

4. Catalytic ozonation process

The catalytic ozonation apparatus used in this study is a home-made system as shown in Figure 10. Ozone is delivered through the use of an ozone generator (Type COM-AD-01, Anseros) supplied by an oxygen tank. By setting the ozone generator at 100% of its full power (29 W) and by the use of a mass flow controller (MFC), ozone is sent to a bubbler containing 20 mL of ultrapure water with pyruvic acid (98%, Alfa Aesar) at concentrations ranging from 0.15 to 0.6 mmol·L⁻¹. The ozone concentration in the liquid phase was followed online using optical fibers (Ocean Optics Maya Pro 2000) with an UV detection set at the wavelength of 259 nm (Deuterium lamp). Considering Beer-Lambert’s law (εO₃ = 3300 L·mol⁻¹·cm⁻¹) the determined concentration of dissolved ozone was of 0.35 mmol·L⁻¹, when the system reached thermodynamic equilibrium.
In order to have a controlled flow rate of 3.6 mL•h⁻¹, a syringe pump (KD Scientific - KDS Legato 210) sucks the solution through the channel and 3.6 mL of the treated solution is recovered in the syringe. The ozone reaction was stopped downstream by adding 130 µL of 10 mmol•L⁻¹ tert-Butanol (99.9%, VWR) solution to rapidly consume any unreacted O₃. The magnetic stirrer ensures the homogenization between the tert-Butanol and the incoming flow arriving in the syringe. Pyruvic acid concentrations before and after reaction were performed by the use of High Performance Liquid Chromatography (HPLC).

Figure n°10: Scheme of the experimental set-up for catalytic ozonation.

5. Analytical methods
5.1 Surface characterizations
5.1.1 FTIR-ATR
Infrared spectroscopy reveals the nature of the chemical bonds present on the surface of a sample. The principle of FTIR relies on the irradiation of the sample with an infrared light source. IR light is sent with a modulator that splits the infrared light into different wavelengths. At the other end of the instrument, a detector measures the amount of absorbed IR light. By data processing, a mathematical function (Fourier transform) is then applied on the collected signal and the absorbed wavelengths can be observed.

The absorbed wavelengths correspond to the vibrational frequencies of the chemical bonds between two atoms. Indeed, when exposed to infrared radiation,
molecules of the sample selectively absorb radiation at given wavelengths which induce their change of dipole moment. The vibrational energy levels of these molecules transfer from the ground state to an excited state. The frequency of the absorption peak is determined by the vibrational energy gap whereas the number of absorption peaks is related to the number of vibrational freedom of the molecules present on the surface of the sample. The intensity of absorption peaks is related to the change of dipole moment and the possibility of the transition of energy levels.

In conjunction with infrared spectroscopy, the use of attenuated total reflectance (ATR) enables the analysis of thin films on a substrate without further preparation. Infrared spectra were acquired using a Fourier-Transform Infrared Spectrometer (Cary 660 Spectrometer-Agilent) displayed in Figure 11, with an Attenuated Total Reflectance module (GladiATR-Pike) at wavenumbers ranging from 600 cm\(^{-1}\) to 4000 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\).

![Figure n°11: Picture of the FTIR-ATR apparatus (Agilent).](image)

### 5.1.2 Water contact angle measurements

Water contact angle (WCA) measurements are performed to assess the wetting properties of a surface. The change of the surface properties of a coated sample in terms of hydrophobicity/hydrophilicity reflects the aging of the studied surface.
Chapter 2: Materials and methods

The contact angle method allows access to the free energy of a surface. It allows also indicates the polar or non-polar interactions at the liquid-solid interface. The hydrophilic or hydrophobic character of a surface can be deduced from the measured angle. A low value of $\theta$ ($\theta < 90^\circ$) indicates a wettable surface (hydrophilic in case the liquid used is water) whereas a high value ($\theta > 90^\circ$) indicates a nonwettable surface (if the liquid used is water, the surface is said hydrophobic).

The contact angle ($\theta$) is measured between the baseline of the drop of a liquid and the tangent at the drop boundary on a flat solid surface as shown in Figure 12.

The shape of a drop on a solid surface is conditioned by three parameters:

- $\gamma_{LG}$, the surface tension between the liquid and the gas
- $\gamma_{SG}$, the surface tension between the solid and the gas
- $\gamma_{SL}$, the surface tension between the liquid and the solid

These surface tensions are related by Young-Dupré’s equation:

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cdot \cos \theta$$

![Figure n°12: Contact angle measurement principle.](image)

In the present thesis, contact angles of MilliQ-water pendant drops on all substrates were measured using a GBX-3S Digidrop-MCAT instrument. Water droplets of 3 $\mu$L in volume were released from a syringe above the sample surface. Images of droplet formation, captured using a high-resolution camera, were analyzed using an image analysis software (Digidrop). For each treatment, contact angle measurements were performed at a minimum of 3 locations on each sample and a typical deviation of $\pm 5^\circ$ from the mean value was observed. The
reported values in this study correspond to the average of these three measurements.

5.1.3 X-Ray diffraction

X-Ray powder diffraction, or XRD, is a technique used to determine the structural properties of crystalline materials. This method enables the determination of intrinsic parameters of a crystalline material such as the crystalline structure, the number of crystalline phases present, the index of the crystalline phase, the mesh refinement, the grain size and orientation, and the deformations of the crystalline network.

As shown in Figure 13, XRD consists in sending a monochromatic X-ray at a given wavelength on the surface of the sample. The incident beam is reflected by the reticular planes \( \{h,k,l\} \) of the crystalline sample which are separated by an inter-reticular distance \( d \). The incident angle on the surface of the sample is noted \( \theta \).

Due to the induced X-ray radiation at a given frequency, an atom starts to vibrate with the same frequency by spreading the radiation in all directions. For atoms arranged in the crystal, the radiation may undergo constructive or destructive interferences according to the direction. Constructive interferences or diffraction peaks are determined by Bragg's law:

\[
2d \sin \theta = n\lambda
\]

![Figure n°13: Principle of the X-Ray diffraction.](image)
Chapter 2: Materials and methods

Information on the structure is obtained through analysis of:

- The angular position of the diffracted lines, which depend on the geometry of the crystal, the size and shape of the mesh.
- The intensity of the diffracted lines, which depend on the type of atoms, their arrangement in the mesh and their crystallographic orientation.
- The form of diffracted lines, which depend on the instrument, the size of the particles and their deformation.

In the present thesis, analyses were performed on a Pan Analytical-X Pert Pro (Model X’Pert Pro PW30420) XRD instrument at the wavelength of $\lambda = 1.5418$ Å (Cu K$_{\alpha_1}$ radiation).

5.2 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy, or XPS, is a characterization technique used to determine the composition of the extreme surface of a sample (5 to 10 nm in depth). XPS is based on the irradiation of a sample with a monoenergetic X-ray beam. This beam is generated by an electron gun bombarding a metallic target (cathode). Irradiation by photons causes the ionization of the atoms located on the surface of the sample by photoelectric effect.

During the relaxation of the excited atoms, electrons are emitted with an energy equal to the difference of energy between the excited state and the steady state. The energy of X-rays is of the same order than the ionization energy of the core electrons. Thus, electrons of the inner shells are mainly ejected. Measurements are performed by analyzing the kinetic energy $E_k$ of the emitted electrons and the characteristic binding energy is calculated according to Einstein’s relation:

$$E_{\text{binding}} = h\nu - (E_{\text{kinetic}} + \Phi)$$

where the energy of the photons ($h\nu$) depends on the X-ray source and $\Phi$, which is the energy required to extract the electron from the vacuum (considered as negligible), depends on the spectrometer. The energy of the photons depends on the nature of the cathode which can be aluminum (monochromatic) or magnesium.
(polychromatic) with photon energies of respectively, 1486.6 eV and 1253.6 eV. The principle of X-ray photoelectron spectroscopy is presented in Figure 14. Generally, analyses of a sample are performed in two phases: first, a quick analysis called “survey” scans (3 passes) the surface using a wide range of energy (from 0 to 1400 eV). The result is a characteristic spectrum of the atoms present on the surface of the sample and relative atomic concentrations of the studied layer can be determined. Thus, pre-identification of specific peaks of desired elements can be carried out in order to obtain, in a second step, a high resolution spectrum. A high-resolution spectrum can identify and quantify the chemical bonds between atoms, by working on a low energy range (typically around 10 eV) in order to increase the resolution of the signal.

![Figure n°14: Principle of X-Ray photoelectron spectroscopy.](image)

Analyses in the present study were performed by Pascale Chevalier at the LBB laboratory (University of Laval, Quebec) with a PHI 5600 XPS spectrophotometer (Physical Electronics, Eden Prairie, MN, USA). Survey and high resolution spectra were acquired using the Kα line of a monochromatic Al (1486.6 eV) and Mg source, respectively, operated at 200 W. Analyses were
Chapter 2: Materials and methods

performed with a 45° angle from the surface. Survey spectra were acquired from 0 to 1400 eV for 15 min. Curve fitting for the high resolution peaks was completed using XPS PEAK Software (version 4.1) by means of a least squares peak fitting procedure using a Gaussian-Lorentzian function and a Shirley baseline fitting. For each sample, three different spots were analyzed and the analyzed surface was 0.8 mm².

5.2.1 Scanning Electron Microscopy

Scanning electron microscopy, or SEM, is a non-destructive analytical technique. The principle is based on the electron-matter interaction and allows obtaining images of a sample in two or three dimensions. This technique uses the transmission of secondary electrons or backscattered electrons from the material. Contrasts of the chemical composition of a material in addition to its morphology can be seen.

SEM is considered as a non-destructive method because it does not alter the surface of the sample. However, it is often necessary to deposit a thin layer of a conductive material (carbon or gold for example) on the sample in order to improve its electrical properties.

An electron incident beam scans the sample surface, giving rise to a spectrum of particles or radiations: secondary electrons, backscattered electrons, Auger electrons or X-rays. More specifically the secondary electrons are created in a shock between the primary electrons contained in the beam and the atoms of the sample: a primary electron can transfer part of its energy to a weak bounded electron in the conduction band of the atom, leading to ionization due to its ejection. These electrons usually have a low energy (about 50 eV) and come from the superficial surface layers of the sample (approximately 10 first nanometers). Compared to secondary electrons, backscattered electrons have a higher energy (up to 50 keV) and come from a higher depth of the sample. These electrons are sensitive to the atomic number of the atoms in the sample: heavier atoms (those having a large number of protons) will emit more electrons than light atoms. This feature is used for the backscattered electrons analysis. Regions formed of atoms
with a high atomic number will appear brighter than others: this is the phase contrast.

SEM was used in the present thesis to assess the morphology of the plasma deposited coatings. A Zeiss Ultra microscope 55 equipped with a thermally assisted field effect electron emission gun was used. This device, available in the Laboratory Interfaces and Electrochemical Systems (LISE) of the University Pierre et Marie Curie (Paris, France), provides images with a resolution down to a nanometer. The field emission gun uses a metallic cathode and applies a voltage ranging from 2 to 7 kV between the tip and the anode. This allows the production of a very high electric field (about 107 V·cm$^{-1}$) at the end of the cathode.

5.2.2 Transmission Electron Microscopy

Transmission Electron Microscopy (or TEM) is an analytical method used to characterize the structure and chemical composition of a solid sample. TEM consists in positioning an ultra-thin sample on a mesh grid in the middle of the trajectory of an electron beam derived from the cathode. Electrons are accelerated by the means of the electromagnetic lenses and create a monokinetic beam that interacts with the sample. The transmitted electrons constitute signals which are measured by the detector and form an image is formed. The image is magnified and focused onto a CCD camera. The input of transmission electron microscopes to optical ones comes from the wavelength of the accelerated electrons (about 1 picometer) in comparison to the wavelength of the photons of visible light (500 to 800 nm) in optical microscopes, which leads to a better observation of thin films for examples. A JEOL JEM 100CX II instrument was used in the present thesis with a Keenview CCD camera and the source was a tungsten filament with an applied tension of 100kV.
5.2.3 **Specific surface area measurements**

The specific surface area (SSA) of a catalyst is crucial information required in the catalysis field. Specific surface area has to be differentiated from the geometric surface which doesn’t take the porosity of the catalyst into account. SSA represents the total available surface on which a molecule can adsorb and can be measured using the BET (from the name of its inventors: Brunauer, Emmet and Teller) adsorption theory.

The BET method consists in measuring the volume of a gas at the surface of a solid and determining the specific surface area of the solid in square meters per gram of catalyst. The sample is introduced into a capillary tube and undergoes a first desorption and heating step in order to remove any adsorbed atmospheric contaminants, and then the measurement step itself which is usually carried out at the temperature of liquid nitrogen in order to obtain detectable amounts of adsorption.

Based on a kinetic model that considers the surface of a solid like a network of adsorption sites or multilayer, the BET theory is an extension of Irving Langmuir’s monolayer adsorption theory that relies on the following hypotheses:

- All surface sites have the same adsorption energy for the adsorbate (nitrogen or krypton gas) and each active site can be occupied only by one particle.
- The adsorption of a molecule on one site occurs independently of adsorption at neighboring sites.
- Adsorbates form a monolayer.

The BET theory extends Langmuir’s theory to multilayer adsorption with the following assumptions:

- Gas molecules physically adsorb on a solid in infinite layers
- There is no interactions between each adsorption layer
- Langmuir’s theory can be applied to each layer
These assumptions lead to the following isotherm equation:

\[
\frac{1}{V_a[(\frac{P_0}{P}) - 1]} = \frac{c - 1}{V_m c \left(\frac{P}{P_0}\right)} + \frac{1}{V_m c}
\]

Where:

- \(V_a\): volume of adsorbate at standard temperature and pressure, in mL
- \(P/P_0\): relative pressure of adsorbate
- \(V_m\): volume of adsorbate as a monolayer on the surface of the sample, in mL
- \(C\): BET constant

The equation of his isotherm requires linear plotting of \(1/(W[(P_0/P) - 1])\) against \(P/P_0\):

With \(s = \frac{c - 1}{V_m c}\) and \(i = \frac{1}{V_m c}\), where \(s\) represents the slope of the curve and \(i\), the y-intercept.

From these values, the volume of adsorbed gas and the BET constant can be deduced receptively from the slope and the y-intercept as:

\[
c = \frac{s}{i} + 1
\]

\[
V_m = \frac{1}{s + i}
\]

The total specific surface area can be calculated as following:

\[
S_{total} = \frac{V_m \times N_A \times S}{V}
\]

\[
S_{BET} = \frac{S_{total}}{m}
\]

With:

- \(N_A\): Avogadro’s constant \((6,022 \cdot 10^{23} \text{ mol}^{-1})\)
- \(S\): adsorption surface of the sample in cm²
Chapter 2: Materials and methods

- V: molar volume of the adsorbate at standard temperature and pressure, in mL\textbullet\text{mol}
- m: mass of the catalyst

Specific surface area measurements were performed by Philippe Barboux at the LCMCP (IRCP, Paris) using a Belsorp-Max apparatus (Figure 15) and by using Krypton as the adsorbate.

![Figure n°15: Picture of the Belsorp-Max apparatus (Bel Japan).](image)

5.3 Analytical methods used for the liquid phases

5.3.1 High Performance Liquid Chromatography

High Performance Liquid Chromatography (HPLC) is a separation technique that enables the identification and quantification of the components in a liquid mixture. The separation relies on the relative polar affinity of the components with either the mobile phase (eluent) or the stationary phase (column).

The HPLC system is based on three main parts:
- The stationary phase or the HPLC column, which is generally made of a silica gel that might be rendered non-polar by grafting hydrophobic groups.
- The mobile phase or the eluent, which can be polar or non-polar depending on the type of column used. Generally, a non-polar column is used with a polar mobile phase and reverse. The mobile phase moves through the
chromatography column (the stationary phase) where the sample interacts with the stationary phase and is separated.

- The detector: once the components are separated, the identification can be done by using a UV-visible detector. The analysis is done at wavelength in accordance with the desired products. Therefore, a reference sample must be injected in order to determine the corresponding wavelength and retention time.

A normal-phase chromatography was used in the present thesis (the stationary phase is polar in opposition to a reverse-phase chromatography where the stationary phase is non-polar). The column is a 4.6 x 250 mm Supelcogel H column for organic acids (Sigma-Aldrich, France) containing sulfonated polystyrene and divinylbenzene particles (9 µm of diameter). The mobile phase is MilliQ water acidified with 0.1 % of orthophosphoric acid. Injections were performed using an automatic injector (Jasco) with an injected volume of 20 µL. The parameters used for the HPLC analysis are summarized in Table 3.

**Table n° 3: Parameters used for the HPLC analyzes.**

<table>
<thead>
<tr>
<th>Mode</th>
<th>Isocratic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate</td>
<td>0.1 mL•mn⁻¹</td>
</tr>
<tr>
<td>Pressure</td>
<td>30 bars</td>
</tr>
<tr>
<td>Wavelength</td>
<td>210 nm</td>
</tr>
<tr>
<td>Analysis time</td>
<td>40 mn</td>
</tr>
</tbody>
</table>
Chapter 2: Materials and methods

Figure n°16: Calibration curve for pyruvic acid (left). Picture of the HPLC apparatus (right).

5.3.2 Flame Atomic Absorption Spectroscopy

Flame Atomic Absorption Spectroscopy, or FAAS, enables the qualitative and quantitative measurements of metallic species present in solution. This analytical technique uses optical methods (Beer-Lambert’s law) and is based on the absorption of photons emitted by ground state atoms.

As shown in Figure 17, the sample is introduced into a graphite furnace (atomizer) and undergoes three steps: drying, decomposition and atomization. During the atomizing step (combustion), the furnace reaches high temperatures (2100 °C to 2800 °C). The light source consists in a hollow cathode made of the element being determined that emits a light beam at a specific wavelength of the desired item. As the sample passes through the flame, the light beam passes through the graphite furnace and is collected by a detector. Atoms in the ground state absorb light at the characteristic wavelengths emitted by the source.

The amount of absorbed light is measured and converted into an electrical signal. This signal is then processed and the amount of the element (concentration of the element in the sample) is determined. Prior to measurements, calibration is required according to the desired metallic element. This technique uses mainly samples in liquid form and provides detection limits down to the μg·L⁻¹ order (or ppb for some metallic elements).
In the present thesis, samples collected after catalytic ozonation in microreactors were analyzed using a Thermo Scientific unit (model 989 QZ Sollar). Analyses of cobalt and iron in solution were performed by Emmanuel Aubry at the BIOEMCO laboratory (UPMC, Paris).

**Figure n°17**: Scheme of the FAAS apparatus.

### 5.3.3 pH-metry

In order to follow the variation of the concentration of protons (H$^+$), pH of the initial and treated solutions were measured using a Mettler Toledo pH meter with an Inlab 418 electrode.