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Escuela de Ciencias Químicas e Ingeniería

TÍTULO: Synthesis and Characterization of Nanocompositebased Electrode: A Preliminary Evaluation of Their Capabilities for the Photo-assisted Electrochemical Degradation of Contaminants.

Trabajo de integración curricular presentado como requisito para la obtención del título de Química

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Dedication

To George, Laura, María Isabel and Juan. This is just the beginning.

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María José Cruz

Resumen

El presente trabajo se inició con la polimerización oxidativa de la polianilina (PANI), en su estado conductor llamado Sal Emeraldina. Este polímero conductor fue usado como la matriz donde se realizó la síntesis de los compositos basados en nanotubos de carbono funcionalizados (fCNTs) y nanotubos de carbono dopados con nanopartículas de dioxido de titania (TiO₂). Estos compositos fueron caracterizados por una serie de técnicas analíticas las cuales incluyen DRX, TEM, UV-Vis NIR y FT-IR para dar a conocer la morfología, tamaño de partícula, propiedades cristalográficas y ópticas. Para la evaluación de la actividad fotocatalítica enfocada en la degradación de contaminantes orgánicos, la constante de velocidad estándar de transferencia electrónica de una catálisis heterogénea se calculó usando voltametría cíclica y además fue comparada con los valores de la resistencia a la transferencia de carga (R_{CT}) estimados a partir de la Espectroscopía de Impedancia Electroquímica. Las comparaciones realizadas entre los diferentes compositos se dieron a cabo usando un sistema redox quasi-reversible de $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$. En este trabajo se calculó el valor de k^0 para cada composito de PANI, fCNTs/PANI, and CNTs-TiO₂/PANI bajo condiciones de luz, oscuridad e irradiación UV mediante el tratamiento propuesto por Nicholson-Kochi basado en la diferencia de potencial entre pico anódico y catódico de los voltamogramas. Para ello, se utilizaron los valores de los coeficientes de difusión calculados a partir de la ecuación de Randles-Sevcik. Finalmente, los resultados muestran que mediante voltametría cíclica, k^0 es mayor para el composito de PANI pura con un valor de $(1.5 \pm 0.2) \times 10^{-4}$ cm s⁻¹ y un R_{CT} de 264.2 Ω , sugiriendo un potencial efecto fotocatalítico sobre los compositos basados en fCNTs y CNTs-TiO₂. Sin embargo, el composito basado en CNTs-TiO₂/PANI satisface la degradación bajo irradiación UV, debido a la generación de radicales hidroxilos y superóxidos los cuales promueven la ruptura de los enlaces en los contaminantes orgánicos, como en el caso de los herbicidas basados en glifosato.

Keywords: actividad fotocatalíca, PANI, nanotubos de carbono, TiO₂, constante de velocidad estandar heterogénea.

Abstract

Polyaniline (PANI) was synthesized in its conductive state by oxidative polymerization and used as the matrix for the synthesis of functionalized carbon nanotubes/polyaniline (fCNTs/PANI) and multiwalled carbon nanotube-doped TiO₂ composites. These composites were characterized by a series of analytical techniques including XRD, TEM, UV-Vis NIR, and FT-IR to reveal the morphology, particle size, crystallographic and optical properties of the composites. For the evaluation of the photocatalytic activity focused on the degradation of organic pollutants, the standard heterogeneous electron transfer rate constants (k^0) were estimated by using cyclic voltammetry and also characterized via electrochemical impedance spectroscopy. A comparison between composites was performed using a quasi-reversible redox system of Fe(CN)₆³⁻/Fe(CN)₆⁴⁻. This work has been able to calculate values of k^0 based on the Nicholson-Kochi method using the difference of peak-to-peak potential and the experimental diffusion coefficients calculated by the Randles-Sevcik equation. Final results show that the PANI electrode got the highest k^0 suggesting a potential photocatalytic effect with a value of (1.5 ± 0.2) x 10^{-4} cm s⁻¹ with a $R_{CT} = 264.2 \Omega$ over, fCNTs/PANI, and CNTs-TiO₂/PANI composites. Nevertheless, CNTs-TiO₂/PANI composite also accomplishes to satisfy the degradation parameter. TiO₂ nanoparticles assist photocatalytic degradation due to its generation of superoxide and hydroxyl radicals that promote bond cleavage in organic pollutants.

Keywords: photocatalytic activity, PANI, carbon nanotubes, TiO₂ nanoparticles, standard heterogeneous rate constant.

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Chapter 1

General Introduction

1.1 Introduction

Nowadays, the increasing use of pesticides due to the development of agricultural techniques¹ has raised environmental concern because of their harmful effects on soil, aquatic microorganisms,² and human health. One of the current problems is the cleaning of pesticide/herbicide containers, which lead to the contamination of ground and underground waters. Thereby, the effects of organic pollutants in the environment and the development of remediation techniques for removing organic pollutants became a real concern for the scientific community. The most common degradation pathways are via adsorption and chemical methods. Nevertheless, the adsorption requires additional steps due to the recovery or destruction of adsorbents, while chemical methods often result in incomplete removal of pollutants or not desirable side products. Thus, the combination of both processes must result in the outstanding removal of pollutants from a specific environment. Consequently, efficient nanocomposite structures have been developed for its photocatalytic degradation in aqueous solutions via electrochemical methods.

Photocatalysis is the most effective method of dealing with wastewater. For environmental applications, oxide semiconductor catalysts have been widely used due to its biological and chemical inertness, strong

oxidizing power, lower cost, and long-term stability against photo corrosion and chemical corrosion.

Semiconductors can supply charges for redox processes induced by light sources due to their electronic formation. They are distinguished by a filled valence band and an empty conduction band, such as TiO_2 . In order to initiate the redox reaction, TiO_2 is irradiated with light that has enough energy to overcome the bandgap, creating electron-hole pairs. However, solar energy is not sufficient to carry out the photocatalytic reaction because the adsorption wavelength of TiO_2 absorbs in the UV region. UV makes up just 8% of the total solar radiation. Further, this process is limited by low interfacial transfer rates of charge carriers and fast charge-carrier recombination.³

In order to overcome the drawbacks, several methods, such as doping, co-deposition of metals, surface chelating, mixing of two semiconductors, coating of an insulating oxide layer, has been used to decrease the charge recombination and increase the TiO_2 photocatalytic efficiency.⁴

Composites of multiwalled carbon nanotubes (MWCNTs) have demonstrated to be more active due to their remarkable properties, including mechanical, thermal, electrical, and elastic properties. Thus, the introduction of MWCNTs improves the electron transfer and the photocatalytic efficiency of TiO_2 because the electrons formed by UV irradiation are easily transported into the conduction band of TiO_2 through the surface of the MWCNTs.⁵ These composite materials can be fabricated by mechanical mixing of TiO_2 and CNTs, sol-gel synthesis of TiO_2 in the presence of CNTs, electro-spinning methods, electrophoretic deposition, and chemical vapor deposition.

Among various conducting polymers, polyaniline (PANI) and polypyrrole (PPy) are the most popular. According to the Web of Science, more than 10,000 papers appeared in the past 30 years on various aspects of chemistry, physics, and engineering of PANI.⁶ This is due to the relatively low cost, availability of raw materials for its synthesis, and because of its doping/dedoping behavior during redox processes. However, the redox sites in the polymer backbone are not stable enough during the charge/discharge process. This problem is solved by hybridizing with inorganic materials such as metal oxides or hydroxides in order to prepare a composite with a higher conductivity, better cyclability, greater capacitance, and mechanical stability. For a low-cost fabrication, metal oxides such as Fe₃O₄, TiO₂, MnO₂, NiO, ZnO, and SnO₂ can improve the capacitance of the PANI-based electrodes while being environmentally friendly.

1.2 Problem Statement

The lack of soil and wastewater treatments due to the contamination of organic compounds originated this study to focus on the synthesis of composites that meet accomplish two specific goals: having a high photocatalytic activity versus other composites and being able to generate oxidizing agents strong enough to promote the degradation of organic pollutants.

The main challenge in this strategy is associated with the synthesis of a composite that fulfills both criteria. This synthesis must take into account the concentration of the metal in the composite, homogeneous distribution, the use of affordable conductive polymers, and the stability of the nanoparticles with the polymer. For this, PANI, fCNTs/PANI, and CNTs-TiO₂/PANI composites were evaluated by electrochemical techniques with their respective chemical and physical characterizations in order to analyze the performance and contribution of the carbon nanotubes, and the nanoparticles of TiO₂ on the polymer focused on photocatalysis and degradation of organic pollutants.

1.3 General and Specific Objectives

This work aims to design electrodes based on PANI doped with functionalized carbon nanotubes (fCTNs) and MWCNTs doped with TiO_2 nanoparticles. The electrodes will be used for further evaluation of the potential photocatalytic activity of each composite by the study of kinetic parameters. This study

will be done under illumination by daylight, UV illumination and without illumination¹ conditions for the potential application on the degradation of organic pollutants.

For the development of these electrodes and their characterization, the following specific objectives are defined:

- Preparation of the polyaniline in the emeraldine salt oxidation state by chemical polymerization.
- Synthesis and characterization of fCNTs and MWCNTs doped with TiO₂ via XRD, TEM, and FT-IR techniques.
- Synthesis of fCNTs/PANI and CNTs-TiO₂/PANI composites for the modification of glassy carbon electrode.
- Cyclic voltammetric and electrochemical impedance spectroscopy study of the electrodes under dark, daylight, and UV illumination conditions.
- Calculation of experimental diffusion coefficients of each electrode system and the standard heterogeneous rate constants for the determination of the composite with the most considerable photocatalytic activity.
- A suggestion of reaction mechanism for CNTs-TiO₂/PANI under UV radiation.

¹Conditions under which the electrode was subjected to daylight irradiation and UV irradiation will henceforth be called "light" and "UV". Conditions under the exclusion of any type of irradiation will be called "dark".

Chapter 2

Theoretical Background

2.1 Materials

2.1.1 Nanostructured materials

Nanomaterials are defined as materials composed of unbound particles or as particles in an aggregate or agglomerate state with one or more external dimensions with a size ranging from 1 to 100 nm.⁷ They are made to take advantage of unique physical and chemical properties that exist at the nanoscale which differ from those of their larger-scale particles.⁸ These emergent properties have the potential for great impacts such as in environmental remediation. Their composites with polymers are used for the detection and removal of gases, contaminated chemicals, heavy metals, organic pollutants and biological substances.⁹

Recent advances for treatment of waste water are nowadays highlighted. This is because the high surface area to-mass ratio of nanomaterials that has improved absorption capabilities. Several engineered nanomaterials are used for those purposes including chitosan, silver nanoparticles, photocatalytic TiO₂, and carbon nanotubes (CNTs). They are widely used as part of environmental remediation technologies. Those methods include the use of ozone, UV radiation, H_2O_2 oxidation, photocatalytic degradation, supercritical

water oxidation, the Fenton method, electrochemical methods, enzymatic treatment methods and others.⁹

Carbon Nanotubes

In the field of nanotechnology, carbon nanotubes (CNTs) represent a promising group of nanostructured materials exhibiting outstanding structural, chemical, mechanical, thermal, optical and electronic properties.¹⁰ They are composed of carbon atoms linked in hexagonal shapes with each carbon atom bonded to three other carbon atoms.¹¹ CNTs are formed by rolling up a single sheet of graphene into a seamless cylinder with diameter of the order of nanometers showing an entirely sp₂ hybridized carbon atoms.¹²

They are classified into single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). SWCNTs are hollow, long cylinders with extremely large aspect ratios, ¹³ and MWCNTs can be considered as multiple rolled up graphene sheets. ¹² Structures are shown in Fig. 2.1.



Figure 2.1: From left to right: Structure of single-walled carbon nanotube and multi-walled carbon nanotube.

Due to the weaker intermolecular forces, the agglomeration of CNTs is one of the frequent problems associated to these nanotubes. It leads to a difficult dispersion in solvents and polymeric mediums. In order to overcome this issue, functionalization of CNTs is carried out by introducing a functional group onto the side chains of the CNTs. It improves the dispersion and reactivity with other materials avoiding bundle formation or agglomeration. CNTs can go through non-covalent or covalent functionalization using surfactants or acids, and physical dispersion by ultrasonication.¹⁴

2.1.2 Titanium Dioxide

Titanium dioxide nanoparticles in the form of anatase have received considerable attention for the ability to remove pollutants through photocatalysis.¹⁵ TiO₂ is a semiconductor that behave as photocatalysts when irradiated by ultraviolet (UV) light in the presence of gas or liquid.¹⁶ It is well-known due to its interesting properties which include stability, non-toxicity, biocompatibility, optical and electrical properties.¹⁷ The advantage of utilizing TiO₂ includes its low cost, radiation stability, and the fact that there is no need to use strong oxidizing agents, such as O₃ or H₂O₂.¹⁸

Nano-sized titanium dioxide has been proved that have high activity in photodegradation process of organic and inorganic contaminants in water¹⁷ under normal conditions of temperature and pressure. It is capable of degrading pollutants such as herbicides, carboxylic acids and alcohols completely to carbon dioxide, water and simple minerals.¹⁹ Titanium dioxide exists in three dimensional crystalline structures namely anatase, rutile and brookite¹⁵ as it is shown in Fig.2.2. In the anatase form, photoactivity is reportedly most pronounced at planes 001.²⁰ It is shown that anatase is more efficient as a photocatalyst than rutile²¹ that is because rutile has a higher electron-hole recombination rate and also it is affected by its preparation conditions.



Figure 2.2: Three main minerals of TiO₂: Anatase, Rutile and Brookite

2.1.3 Conducting Polymers

Conducting polymers (CPs) are an exciting new type of electronic materials, which have attracted the interest since their discovery in 1977²² induced by reversibly doping processes. They are mainly unsaturated polymers with electrons that can be added or removed from its chain by redox processes.²³ Classical CPs are copolymerized, mixed with graphene or charged with nanotubes, clays, zeolites, and other constituents yielding materials that combine the advantages²⁴ and properties of each component enriching its unique characteristics. The use of conducting polymers as photosensitizers enhance photocatalytic activity which is not possible with semiconductors alone because of its inadequate response to visible light, high rate of electron-hole recombination, leaching, and thermal decomposition.²⁵

Polyaniline

PANI exhibits semiconducting behavior because of extended π -conjugation along the polymeric backbone.²⁶ Currently, polyaniline in its base form consists of two central structural units i.e., the benzenoid diamine and the quinoid diimine. It is represented schematically by the following formula as shown in Fig. 2.3.



Figure 2.3: General Structure of PANI built from reduced (n) and oxidized form (1-n) blocks

PANI can store electrical energy through its redox transitions.²⁷ It exists in three idealized oxidation states: the completely reduced form, leucoemeraldine (n=1), the completely oxidized form, pernigraniline (n=0), and the partially oxidized form, emeraldine (n=0.5). Fig. 2.4 shows the redox reactions of PANI. In acidic conditions, the emeraldine forms a green salt becoming the single conductive state of this polymer.



Figure 2.4: Redox reaction of PANI

The synthesis of emeraldine salt (ES) undergoes chemical and electrochemical methods in order to obtain electroactive and conducting composite materials.²⁸ ES goes through the intramolecular mechanism from the emeraldine base. In acidic conditions of the emeraldine base, protons interact with the nitrogens of the imines resulting in the formation of polycations. These positive charges increase the total energy of the polymer providing its electron conductivity. However, the delocalization of cation radicals can also occur via the intermolecular mechanism. In this case, polymer chains are oriented in a direction where π -electrons are transferred from one polymer chain to another. Interactions between benzene and quinoid rings are of van der Waals's nature.

In the solid-state powder, PANI has a tendency to aggregate due to the interchain hydrogen-bonding²⁹ reducing its solubility. Therefore, ES is just dispersible but not soluble.³⁰ For particle dispersion, polar solvents are used to lower the surface tension of the polymer and to disrupt its aggregation forming an expanded coil conformation. Typical solvents used are dimethyl sulfoxide (DMSO)³¹, m-cresol³⁰, and dimethylformamide (DMF).

2.2 Electrochemical Characterization Techniques

Electrochemistry deals with the phenomena of charge transfer, which occur homogeneously in solutions or heterogeneously at electrode/solution interfaces.³² Electrochemistry manages methods for measurement of electrochemical phenomena that relate chemical reactions (kinetics) to an applied potential or current. Most of these techniques are based on the measurement of electrolytic current and electrode potential. This section gives an overview of electrochemical techniques, their principles, and their latest information.

2.2.1 Linear Sweep Voltammetry

In linear sweep voltammetry (LSV), the electrode potential is varied at a constant rate throughout the scan, and the resulting current is measured. This voltage is scanned from a lower to an upper limit.³³ The voltage scan rate is calculated from the slope of the line, as shows in Fig 2.5.



Figure 2.5: Linear Sweep Voltammogram.

In LSV measurements, the current is plotted as a function of voltage, which is called a voltammogram. As voltage is swept further to more reductive values, current begins to flow and reaches a peak where the diffusion layer has grown enough above the electrode so that the flux of reactant to the electrode is not fast enough to satisfy that required by the Nernst equation.

2.2.2 Cyclic voltammetry

Cyclic voltammetry consists of cycling the potential of an electrode. This electrode is immersed in a solution, which maintains unstirred, measuring the resulting current. Potential is applied between the working electrode and the reference electrode.

This potential can be considered as an excitation signal until it reaches a limit, called the switching potential, which is represented as point C at Fig.2.6. At this value, the scan is reversed, and after this point, a second cycle starts. It has a triangular waveform resulting from linear behavior. During the potential scan, cyclic voltammogram is obtained by the current measured at the working electrode. This current can be considered as the response signal.³⁴



Figure 2.6: Excitation signal for cyclic voltammetry with a triangular potential waveform.

In the overall process, the current depends on the movement of electroactive material to the electrode surface and the electron transfer reaction. Electron transfer rate constant k_0 for a reduction process can be described by Eq. 2.1:

$$k_0 = k^0 exp\left[\frac{-\alpha nF}{RT}(E - E^{0'})\right]$$
(2.1)

where k^0 is the standard heterogeneous electron transfer rate constant, α is the transfer coefficient, *n* is the number of electrons transferred in the redox event, *F* is the Faraday constant, *R* is the universal gas constant, *T* is Kelvin temperature and $E^{0'}$ is the formal reduction potential.

Equilibrium between oxidized and reduced species is described by the Nersnt equation (Eq. 2.2). It relates the potential of an electrochemical cell to the standard potential and the activities of the oxidized and reduced species at the equilibrium. It predicts how a system will respond to a change in the activities of species in solution or a change in the electrode potential.³⁵

$$E = E^0 + \frac{RT}{nF} ln \frac{a_{Ox}}{a_{Red}}$$
(2.2)

Electrochemical reversibility refers to the kinetic between the electrode and the redox species. For electrochemically reversible electron transfer processes that involve freely diffusing redox species, the Randles-Sevcik equation (Eq. 2.3) describes how the peak current i_p (A) is proportional to the square root of the scan rate v (V s⁻¹). It is mainly used for calculating diffusion coefficients.

$$i_p = 0.4463nFAC^0 \frac{nFvD_0}{RT}^{1/2}$$
(2.3)

where A (cm²) is the electrode surface area, D^0 (cm² s⁻¹) is the diffusion coefficient of the oxidized analyte, and C^0 (mol cm⁻³) is the bulk concentration of the analyte. Deviations from linearity are referred to the electrochemical quasi-reversibility of as the system or surface-adsorbed mechanism in electron transfer.

2.2.3 Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is based on the alternating current (AC) response as a function of the frequency of an imposed potential signal. It is carried out through a potentiostat and a frequency response analyzer (FRA) with a 2–or 3–electrode configuration. Impedance (Z) is defined as a linear time-invariant system, which shows three conditions: causality, stability, and finiteness.

Causality means that system response must depend only on AC voltage and not from other stimulus. Stability means that the system has to depend on the stationary state before and after a perturbation. Finiteness means that both real and imaginary impedance values have to be finite over the whole frequency range. These kinds of systems are intrinsically not linear, but under a low potential excitation amplitude value, electrochemical systems are considered pseudo-linear in the region of the current-voltage curve. These values lie on the range from 10 to 100 mV³⁶ and frequency values lie on the range from MHz to mHz. Impedance is related to Ohm's law (Eq. 2.4) by:

$$Z(\omega, t) = \frac{V(\omega, t)}{I(\omega, t)}$$
(2.4)

By applying Euler's relationship:

$$Z(\omega, t) = Z'(\omega) + jZ''(\omega)$$
(2.5)

where Z' and Z'' are the real and imaginary part of the impedance, respectively. Usually, experimental data are represented with the Nyquist and Bode plots. Nyquist plot reports Z'' as a function of Z' in the complex plane, as it is shown in Fig. 2.7 part b. Since Nyquist plots mask the impedance dependence on frequency, sometimes data is plotted using the Bode plot. Bode plot reports $\log |Z|$ and θ as a function of frequency (Fig. 2.7 part c). Data is then interpreted using equivalent circuits made of resistors, capacitors, constant phase element, and Warbug resistances (Fig. 2.7(a)). For modeling systems, computer-assisted processes are carried out by software packages such as EIS Analyzer.


Figure 2.7: (a) Simplified Randles circuit, (b) Nyquist plot and (c) Bode plot for one electron transfer reaction.

The analysis of EIS data begins by fitting it to an adequate equivalent circuit model. The interpretation and modeling of data are of high subjectivity, suggesting that there may be several circuit models that fit the same EIS data set.³⁷ Despite this, every element in the circuit should have a basis in the physical chemistry of the system.³⁸ Finally, another limitation includes the fact that they neglect ion diffusion and nonuniform ion concentrations in the electrolyte.³⁹ Table 2.1 lists common circuit elements, their equations and symbols.

Element	Units	Symbol	Impedance
Resistor (<i>R</i>)	Ω		Z = R
Capacitor (C)	F		1/(jωc)
Constant Phase Element (CPE)	F	$\rightarrow \rightarrow$	$Y_0(jw^n)$
Warbug Resistance (W_R)	Ω		$\sigma/\omega^{1/2} - j\sigma/\omega^{1/2}$

Table 2.1: Most common equivalent circuits elements with their respective symbols and impedances.

In many cases, a simplified Randles circuit is considered as a starting point for an electrochemical

system. This circuit includes a solution resistance R_S , a double layer capacitor C_{DL} and a charge transfer resistance R_{CT} or polarization resistance R_P . R_S is the resistance between the working electrode and the reference electrode. C_{DL} represents the double layer formed at the interface between the electrode and the electrolyte solution. The charges from the electrode and the ions in solution are separated in the Helmholtz-layer, acting as a capacitor. Charge transfer resistances are originated from the electronic and ionic resistance at the electrode-electrolyte interface. Finally, the Warbug resistance W_R is related to the resistance of ionic diffusion in the electrolyte.⁴⁰

2.3 Other Experimental Techniques

X-ray Diffraction (XRD)

XRD is a non-destructive technique that provides information about the crystallographic structure, chemical composition, and physical properties of a material.⁴¹ A monochromatic beam of X-rays is projected into a sample and then the scattered X-rays are detected.⁴² These scattered rays interfere with each other,⁴³ and are studied by using Braggs's Law ($n\lambda = 2d \sin \theta$). Peak angles are used to determine particle size and the degree of crystallization.⁴⁴ Crystalline regions of samples are only observed when the diffraction lines are very narrow, while amorphous regions produce broad peaks in the diffractogram.⁴²

Transmission Electron Microscopy (TEM)

TEM is a technique that uses a high-energy electron beam that is transmitted to a sample to form an image.⁴⁵ It directly measures grain size, distribution and morphology of particles.⁴⁶

Scanning Electron Microscopy (SEM)

SEM is another common technique for imaging structure and morphology of materials.⁴⁷ The main difference with TEM is that SEM scans the surface of a material with a low-energy electron beam. It gives information about the topography of samples over a broad range of magnification.⁴⁸ Performing and EDX

(Energy dispersive X-ray spectroscopy) contributes to the analysis of the composition and distribution of particles for polymers that can helps improving the dispersion process.⁴⁹

Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR is also a non-destructive technique used for the determination of different functional groups⁵⁰ and types of chemical bonds present in a molecule.[?] It measures the interaction of infrared radiation with a sample by producing an infrared absorption spectrum as a molecular "fingerprint."⁵¹

Ultraviolet-Visible Spectroscopy (UV-Vis)

UV-Vis is another technique that has been extensively used to study the optical properties of compounds.⁵² It helps to understand the interaction between the polymeric matrix and nanofillers in a nanocomposite.⁵³ The amount of radiation is related to the concentration of the analyte solution. This relationship is known as Lambert-Beer Law ($A = \varepsilon cl$), where A is the absorbance, ε is the molar absorption coefficient, c is the molar concentration and l is the optical path length. In this method, carbon nanotubes are usually found in the near infrared visible ultraviolet⁵⁴ (NIR UV-Vis).

Chapter 3

Methodology

3.1 Reagents and solutions

Materials

Aniline monomer was purified by simple distillation at 165°C to remove any impurities and oligomers. Ammonium persulfate (APS, \geq 98.0%), hydrochloric acid (HCl, 36% - 38%), sulfuric acid (H₂SO₄, 95.0 - 97.0%), potassium phosphate monobasic (KH₂PO₄, \geq 99.9%), sodium hydroxide pellets (NaOH, \geq 97.0%), sodium nitrate (NaNO₃, \geq 99.0%), potassium ferrycianide (K₃ [Fe(CN)₆], \leq 10 µm, \geq 99.0%) and dimethyl sulfoxide (DMSO, anhydrous, \geq 99.0%) were purchased from Sigma Aldrich and used as received. Pristine multi-walled carbon nanotubes (pMWCNTs) were obtained from Nanocyl S.A. Functionalized carbon nanotubes and carbon nanotubes doped with TiO₂ nanoparticles were synthetized and characterized at Instituto Venezolano de Investigaciones Científicas, Venezuela, and used as received. Glyphosate (isopropylammonium salt) herbicide was used as the commercial formulation of Ranger[®] 480 EC. All other reagents were of analytical reagent grade used without further purification. Milli-Q quality water was used for washing, rinsing and the preparation of all solutions.

1 M Sulfuric Acid solution

For electrode polishing procedure, 1 M sulfuric acid solution was prepared by diluting 1.33 mL of concentrated H₂SO₄ in 25 mL of Milli-Q quality water.

0.5 M Sodium Nitrate solution

0.5 M sodium nitrate solution was prepared by dissolving 4.25 g NaNO₃ in 50 mL of Milli-Q quality water.

5 mM Potassium Ferricyanide solution

5 mM potassium ferricyanide solution was prepared by dissolving 41.16 mg of K₃ [Fe(CN)₆] in 25 mL of PBS pH 7 for running each electrochemical experiment.

10 mM Glyphosate-based herbicide solution

10 mM glyphosate-based herbicide solution was prepared by $72.2 \,\mu\text{L}$ of herbicide in 100 mL Milli-Q quality water. Calculation was performed assuming that glyphosate was present as isopropylammonium salt at $48 \,\text{g L}^{-1}$.

Polyaniline synthesis

PANI was prepared by chemical polymerization. After simple distillation of aniline, 0.325 M solution was prepared by dissolving 3 mL of pre-cooled monomer in 7.7 mL 1 M HCl solution. As a reducing agent, an equal-volume solution of 0.125 M APS was prepared with 2.85 g of APS in Milli-Q quality water. APS solution is added gradually to the monomer under constant stirring. During this process, temperature was maintained at 5°C by an ice bath. The resulting green suspension was filtered and washed with Milli-Q quality water and methanol until all soluble impurities were removed. Precipitate was then dried for 24 hours at 40°C.

fCNTs/PANI and CNTs-TiO₂/PANI Composite Synthesis

Several methods of synthesis of fCNTs/PANI have been reported for the fabrication of these composites.

They can be synthetized by electrochemical or chemical processing. This composite was manufactured by dispersing functionalized carbon nanotubes in a 0.032 M PANI solution in DMSO. Then, fCNTs and CNTs-TiO₂ 1 wt% dispersions were made in 1 mL of the PANI solution each one. Finally, samples were sonicated for 8 minutes at 25°C in a Stainless Steel Ultrasonic Cleaning Bath, JP Selecta, Spain.

3.2 Electrochemical Cell Design

A standard 3-electrode system was used in all the experiments as the electrochemical cell (EC). Electrodes used for EC ensemble were: a glassy carbon electrode (working electrode), Ag/AgCl electrode (reference electrode) and platinum electrode (counter electrode). Cyclic voltammetry experiments were carried out with 25 mL of solution. In the system, the separation between the working electrode and the reference electrode was about 1 cm. A schematic representation of an electrochemical cell is presented in Fig. 3.1.



Figure 3.1: Schematic representation of 3-electrode system for the measurements of modified GCE inmersed in electrolyte solution.

For impedance measurements, a graphite electrode was adapted to the electrode system. All electrochemical characterization techniques were performed in an Autolab PGSTAT128N low current and noise with a fast potentiostat/galvanostat⁵⁵ able to measure a maximum of 800 mA equipped with FRA32M impedance spectroscopy module. Experiments were run in Nova 2.1 Metrohm Autolab module (Metrohm, Netherlands).

Glassy Carbon Working Electrode

The unmodified working electrode was a Glassy Carbon Disk Electrode (GCE) with 3 mm electrode diameter and Kel-F as supporting material (model CHI104, CH Instruments, USA).

Silver-Silver Chloride Reference Electrode

The electrode was a commercial Ag/AgCl reference electrode with an electrolyte concentration of 3 M KCl (6.0733.100, Metrohm, Netherlands). The working range of the electrode is 0°C to 80°C.

Platinum Counter Electrode

A platinum rod 2 mm diameter was applied as counter electrode (0092, Metrohm, Netherlands).

UV irradiation chamber

For measurements under dark conditions, the cell was mounted inside a dark box. For UV irradiation, the cell was mounted inside the dark chamber and irradiated with a band centered at 365 nm. The CV experiments were performed in a cell assembly as shown in Fig. 3.2 for the cases of UV-irradiation conditions. The whole chamber is not further used for natural light conditions.

3.3 Carbon Nanotubes and Nanocomposite Characterization

Transmission Electron Microscopy

The TEM images were obtained in a JEOL 1220 microscope of Polymers Laboratory of Simon Bolivar



Figure 3.2: Schematic representation of UV irradiation chamber with wavelength of 365 nm for the 3-electrode system cell.

University (Venezuela) with an accelerating voltage of 100 kV. The samples were prepared using a wet suspension technique with an ethanol/water (70% v/v) solution.

Fourier Transform Infrared Spectroscopy

The spectrum for carbon nanotubes dopped with TiO₂ NPs were performed in a Nicolet iS10 FT-IR spectrometer in Chemistry Center of IVIC. The samples were prepared in KBr pills. The frequency range of spectra goes from 4000 to 400 cm^{-1} with 64 sweeps at 2 cm^{-1} resolution. The spectra for PANI, fCNTs/PANI and CNTs-TiO₂/PANI composites were performed in a Cary 630 FT-IR spectrometer in Yachay Tech University. The samples were used as the dispersion of composites in DMSO. Then, $2.5 \,\mu\text{L}$ was dropped bellow the Cary 360 Diamond ATR Accessory for measurements. Thus, FT-IR is used to evaluate the morphology of MWCNTs and TiO₂ in the composite.⁵⁶ The frequency range of spectra goes from 4000 to 500 cm⁻¹.

X-ray Diffraction

The sample of CNTs-TiO₂ were analyzed via a SIEMENS D5005 diffractometer with a wavelength of 1.54178 Å and a range of $2 = 10^{\circ}$ to 80° with a rate of $0.02^{\circ}/0.52$ s. The data were collected from Laboratory of Environmental Chemistry of IVIC, Venezuela. Data was analyzed in order to determine the

particle size of TiO₂ by the Scherrer equation. It can be written as:

$$\tau = \frac{K\lambda}{\beta\cos\theta} \tag{3.1}$$

where τ is the mean particle size of crystallites, *K* is the dimensionless shape factor which is close to the unity, λ is the X-ray wavelength, β is the line broadening at half the maximum intensity in radians and θ is the Bragg angle.⁵⁷

UV-Vis NIR

The UV-Vis absorption measurements were carried out with a PerkinElmer model Lambda 1050 that works across the UV, Visible and NIR regions of the spectrum. The composites were diluted 50% (v/v) in DMSO using a one-top rectangular absorbance cuvette with a pathlength of 2 mm.

3.4 Electrode Modification

Electrode Polishing

As the redox event occurs at the working electrode surface, it shall be spotless electrode with a very-well defined surface. Therefore, it is necessary to polish the electrode before measurements. For glassy carbon electrodes, the surface is very reactive once activated via polishing.³⁴ Treatment consists of two processes: mechanical and electrochemical polishing.

- 1. A simple way to mechanically polish electrode is in eight-motion on a polishing pad in water-alumina slurry for 3 minutes. After cleaning, the electrode is rinsed with Milli-Q quality water.
- 2. To remove any adsorbed species left from the polishing procedure, several CV scans in a cell containing $25 \text{ mm } 1 \text{ M H}_2\text{SO}_4$ from -1.5 to 1.5 V with a scan rate of 50 mV s^{-1} for 10 cycles were performed.

Glassy Carbon Electrode Modification

After electrode polishing and drying, a suspension of PANI of a volume of $10 \,\mu$ L was pipetted and uniformly dispersed onto the electrode surface via the drop-casting process. The electrode was dried at 40°C for 30 minutes. The same procedure was done with the fCNTs/PANI and CNTs-TiO₂/PANI dispersions over the GCE. Drying time differs from one matrix to another, 1 and 2 hours, respectively. Because of the electrostatic affinity, a binder is not needed to attach those new matrices to the GCE. General procedure is shown in Fig. 3.3.



Figure 3.3: General schematic procedure for the modification of GCE with $CNTs-TiO_2/PANI$ by dropcasting process. The same experiment is performed for PANI and fCNTs/PANI dispersion.

Determination of photocatalytic activity of modified electrodes

Photocatalytic activity detection of composites was accomplished using a 5 mM potassium ferricyanide solution through CV and electrochemical impedance measurements with PANI, fCNTs/PANI and CNTs-TiO₂/PANI composites under UV radiation.

3.5 Electrochemical Characterization

The electrochemical behavior of the electrodes was investigated on NaNO₃ solution using cyclic voltammetry. The first experiment consisted of determining the potential window of the electrolyte by cyclic voltammetry. The potential window is the voltage range where the electrolyte (solvent or supporting salt) is redox inactive.⁵⁸ Outside this range, the solvent (water) gets electrolyzed.⁵⁹ Bare and modified electrodes were immersed into 10 mL of 0.5 M NaNO₃ solution in an electrochemical cell. Cyclic voltammetry was performed over 15 cycles until the current response did not change with each new cycle. Table 3.1 shows the selected parameters for the determination of the potential window. EIS measurements were performed from 10 kHz to 10 mHz at OCP vs Ag/AgCl electrode. A high-frequency shunt with a 1 nF capacitor was used to remove artifact (Fig. 3.4).



Figure 3.4: Schematic representation of the electrode system for the measurements of EIS at bare and modified GCE inmersed in 5 mM K_3 [Fe(CN)₆] in 0.5 M NaNO₃

The reversibility of an electrochemical reaction describes the rate of electron transfer. Potassium ferricyanide was used as the redox probe for electrochemical electrode characterization. It undergoes a one-electron redox process $O + ne^- \rightleftharpoons R$ with no subsequent reactions.⁶⁰ CV study was used for the

	Values		
Parameter	Potential Window	Diffusion Coefficient	
OCP/ V	0	0	
Upper Vertex/ V	2	1.35	
Lower Vertex/ V	-1.8	-1.1	
Number of scans /cycles	15	5	
Scan Rate/ mV s ⁻¹	From 25 to 100	From 5 to 100	
Steps	0.00244	0.00244	

Table 3.1: General parameters for the CV study of potential window and diffusion coefficient for bare and modified electrodes. Potentials are reported against Ag/AgCl reference electrode.

evaluation of quasi-reversibility of the system. Parameters for the experiment are also shown in Table 3.1. Finally, the specific surface area of fCNTs and CNTs-TiO₂ were determined by BET theory analysis via N_2 adsorption.

3.6 Determination of the standard heterogeneous rate constant k^0

The standard rate constant is a measure of the kinetic facility of a redox couple.⁶¹ The larger the k^0 value, the shorter the time that the system will need to achieve equilibrium. The evaluation of the standard heterogeneous rate constant k^0 of electron transfer from CV data is based on the peak-to-peak separation ΔE_p of a redox couple. This data is treated by Nicholson equation (Eq. 3.2) for quasi-reversible systems, which establishes a relationship between Ψ and k^0 .

$$\Psi = k^0 \left[\frac{\pi D n \nu F}{RT} \right]^{-1/2} \tag{3.2}$$

where Ψ is the kinetic parameter. Nicholson introduces Ψ as a dimensionless parameter that is further used as another reversibility analysis criterion, where $\Psi = 20$ indicates a reversible system and $\Psi < 7$, a quasi-reversible one.62

Kinetic parameters are included in the reaction rate equations, such as adsorption equilibrium constants, rate constants, and reaction order. They are obtained by kinetic data from experimental study. Consequently, the accuracy of the kinetic parameters depends only on the quality of the experiments. Therefore, the kinetic parameter must reflect the intrinsic kinetics of the experimental results. To achieve this, heat and mass transfer processes must be eliminated. This indicates that a parameter to consider is a uniform temperature distribution inside the electrochemical cell. Thus, these experiments must be carried out under isothermal conditions.⁶³

However, Nicholson's treatment is valid for ranges between 60 and no more than 200 mV of ΔE_p . In order to deal with the problem, Klinger and Kochi determined a relationship between Ψ and ΔE_p that is valid within much broader ranges of ΔE_p , which is defined by:

$$\Psi = 2.18 \left(\frac{\alpha}{\pi}\right)^{1/2} exp\left(\frac{\alpha^2 F}{RT} n\Delta E_p\right)$$
(3.3)

Eq. 3.3 also considers the electron transfer constant α . This α value is obtained from Eq. 3.4 :

$$E - E_{1/2} = \frac{48 \,\mathrm{mV}}{n\alpha}$$
 (3.4)

where *n* is the number of electrons involved in the redox reaction. In order to determine k^0 , the procedure of Nicholson-Kochi must be applied with the use of a working curve Ψ vs ΔE_p followed by a Ψ vs $\nu^{-1/2}$ plot. From the slope of the plot $\Psi = k^0 [\pi Dn\nu F/RT]^{-1/2}$, the kinetic parameter k^0 can be easily evaluated.⁶⁴

Chapter 4

Results & Discussion

This section will describe the chemical and physical characterization of fCNTs and MWCNTs-TiO₂ samples by XRD, TEM, and FT-IR techniques. PANI and its nanocomposites were characterized by UV-Vis NIR and FT-IR. Then an electrochemical characterization was performed over PANI/GCE, fC-NTs/PANI/GCE and CNTs-TiO₂/PANI/GCE. Composites were investigated via cyclic voltammetry. These experiments gave necessary information for the calculation of diffusion coefficients by the Randles-Sevcik equation. Moreover, the kinetic parameter Ψ was determined to establish the standard heterogeneous rate constant k^0 for each composite under light, dark and UV environmental conditions. Furthermore, electrochemical impedance spectroscopy is used for the construction of equivalent circuits for the composites, giving values for the charge transfer resistance. Finally, k^0 and R_{CT} values were compared to each other for the election of the photocatalytic composite.

4.1 Chemical and Physical Characterization of carbon nanotubes and composites

Crystal Structure

The X-ray diffraction pattern of the oxidized MWCNTs has been reported earlier.⁶⁵ The strong diffraction peak for the samples at the angle 2θ of 25.8° corresponds to the CNT(002) reflection of the hexagonal graphite structure of MWCNTs.⁶⁶ This peak overlaps with the anatase TiO₂ (101) reflection plane at 2θ = 25.3°. Other peaks at the XRD pattern at 37.84° (004), 48.1° (200), 53.7°(105), 62.7° (204) clearly represents the anatase phase, as the major crystal formed in the structure.



Figure 4.1: XRD pattern of CNTs-TiO₂

Diffraction peaks corresponding to rutile or brookite phase were not found. The average crystallite size of TiO_2 nanoparticles on the surface of MWCNTs is estimated by using Scherrer equation (3.1) for

the corresponding X-ray spectral peaks⁶⁷ concluding an average size of 8 nm.

TEM study

Physical characterization by TEM images confirms the morphology and nanostructure of fCNTs and CNTs-TiO₂ nanocomposite. Fig. 4.2 shows bundle formation of nanotubes which has various lengths and diameters. The diameter mean value already reported of fCNTs is 5 nm.⁶⁸



Figure 4.2: TEM image for functionalized carbon nanotubes.

Fig. 4.3 shows the TEM images of CNTs-TiO₂ in where TiO₂ NPs have adhered to the surface of functionalized nanotube walls. It demonstrates that the deposition of the nanoparticles occurred unevenly. It also shows the existence of not very well spread of TiO₂ NPs along the tube walls due to their high surface energy, resulting in their agglomeration on the surface of the nanotubes. This agglomeration of particles can affect the CV and EIS measurements.

However, these results confirm the successful interaction of nanotubes with nanoparticles due to physisorption process, suggesting that TiO₂ NPs may attach to nanotubes surface through van der Waals



interactions and can be detached from it through a mechanical process, such as sonication.⁶⁹

Figure 4.3: TEM images of CNTs doped with TiO_2 at different magnifications.

UV-Vis study

Polyaniline matrix synthesized by oxidative polymerization was subjected to UV-Vis NIR and FT-IR characterization. Fig. 4.4 presents the UV-Vis spectra of both: (a) PANI polymer, (b) the dispersion

of fCNTs/PANI and CNTs-TiO₂/PANI composites. The peak in the region between 270 and 300 nm corresponds to the π - π^* transition of the conjugated moiety. The sharp through 503 nm of the polaron- π^* transition, and the extended tail nearly at 650 nm are characteristic of protonated PANI. Consequently, it confirms the existence of emeraldine salt as the conducting state of PANI.²⁷ For CNTs-TiO₂/PANI composite, it shows a broad peak near 280-290 nm indicating the presence of surface plasmon resonance of TiO₂.⁷⁰ Its absorption increases due to the increment of the amount of TiO₂ from 0.1 to 1 wt% in CNTs-TiO₂/PANI composite. This means that the TiO₂ composite can strongly absorb ultraviolet light more than just with fCNTs, proving that these nanocomposites could have a potential use as photocatalyst material. Fig. 4.4 highlights the principal signals of composites.



Figure 4.4: (a)UV-Vis spectrum for PANI emeraldine salt and (b) UV-Vis spectra for 0.1wt% CNT-TiO₂ (black line), 1wt% CNT-TiO₂ /PANI (red line) and fCNTs/PANI (blue line) nanocomposites.

FT-IR spectra

Figure A.1 demonstrates the FT-IR spectra for the synthetized CNTs-TiO₂ nanocomposite. TiO₂ characteristic bands can be identified from the sample. The broad peak at 3500 cm^{-1} can be attributed to hydroxyl

groups from residual alcohol (Ti-OH) and also to the surface-adsorbed water molecules that are trapped in the oxide network⁷¹ which are coordinated to Ti⁴⁺ cations. The main peak at 580 cm⁻¹ corresponds to Ti-O stretching and Ti-O-Ti bridging stretching modes.⁷² In addition, bands between 2700 and 3000 cm⁻¹ could be attributed to frequencies of residual organic species which has not completely removed by distilled water washing from synthetized TiO₂. Also, they can be related to the anti-symmetric C-H mode of CH₃ bending vibrations due to the presence of CNTs. In fact, modification of band gap energy of TiO₂ and extension of light absorption into the visible region is due to the presence of Ti-O-C bonds which causes reduction of band gap energy for photogenerating of electrons and holes.⁶⁹

The FT-IR spectrum of PANI is shown in Fig. 4.5. It shows bands at 2910 and 2997 cm⁻¹ for amine salt N-H stretching, 1663 cm⁻¹ for C=C stretching of phenyl rings, 1311 cm⁻¹ for C-N stretching bond of aromatic amines. The band at 1016 cm⁻¹ is assigned to an in-plane bending vibration of C–H (mode of N=Q=N, Q= N^+ H=B and B– N^+ H–B), which is formed during protonation of PANI.⁷³ fCNTs/PANI and CNTs-TiO₂/PANI composites show same peaks for amine salt N-H stretching, benzene ring and aromatic amine C-N stretching. For TiO₂ composite, the peak 3422 cm⁻¹ gets broadened due to some moisture absorption thereby O-H stretching frequency.⁷⁴ Also, it shows a slight shift of 1657 cm⁻¹ from the C=C stretching of PANI due to interaction with TiO₂ NPs. Finally, the sharp at 600 cm⁻¹ indicates the Ti-O-Ti stretching frequency confirming the formation of TiO₂ over the polymeric matrix. Results show agreement with earlier reported data.⁷⁵

4.2 Voltammetric Studies

Cyclic voltammetry (CV) is most commonly used to investigate the electrochemical properties of electrolytes and electrode materials.⁷⁶ PANI/GCE, fCNTs/PANI/GCE and CNTs-TiO₂/PANI/GCE nanocomposites were examined using CV. Measurements were conducted in 0.5 M of NaNO₃ within -1.1 to 1.35 V potential range versus Ag/AgCl reference electrode.

Compound	Wavenumber (cm^{-1})	Signal assignment
TiO ₂	3422, 3500	Ti-OH
	580, 600	Ti-O / Ti-O-Ti
fCNTs	2700-3000	C-H antisymmetric
PANI	2910, 2997	N-H stretching
	1663	C=C phenyl ring stretching
	1311	C-N stretching
	1016	C-H in-plane vibrations

Table 4.1: Principal signal frequencies with its respective peak assignment for TiO₂, fCNTs and PANI.



Figure 4.5: FT-IR spectra of PANI, fCNTs/PANI and CNTs-TiO₂/PANI nanocomposites.

4.2.1 Determination of the potential window

The chemical stability of an electrolyte determines the maximum operating voltage that is evaluated by measuring its electrochemical potential window.⁷⁷ It is defined as the potential region in which no appreciable faradic current flows indicating that there is no charge transfer reaction at the electrode.⁷⁸

For the determination of the potential window, it is necessary to select a cut-off current density to evaluate the oxidation and reduction potentials. The potential window can be identified by the cathodic (reduction) and anodic (oxidation) limiting potentials, which can be defined as E_{CL} and E_{AL} , respectively. Both values can change depending on the cut-off current density already arbitrarily defined. These values are selected between 0.1 and 1 mA cm⁻¹.⁵⁸

Fig. 4.6 shows the potential window of the (a) bare GCE, (b) CNTs-TiO₂/PANI/GCE, (c) PANI/GCE and (d) fCNTs/PANI/GCE at a sweep rate of 25 mV s⁻¹. The value of 1 mA cm⁻¹ was selected for the cut-off current density. Therefore, the $E_{AL} = +1.8$ V and $E_{CL} = -1.7$ V. This suggests that the electrolyte have a wide potential window. Consequently, high concentrations of electrolyte solutions are needed.⁵⁸

There are two prominent peaks found over the whole potential for PANI and its corresponding composites at -0.2 V and +0.9 V, respectively. These peaks are attributed to the redox transition of the polymer between the emeraldine and pernigraniline state.⁷⁹ It is important to mention that those peaks must not overlap with the peaks of the ferricyanide solution. Indeed, Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ peaks appear between 0.1 and 0.5 V.

Moreover, fCNTs/PANI/GCE nanocomposite shows a strong increment in the output current, which is much larger than the pure polymer and its composite. This increment corresponds to the non-faradaic current, which does not involve electron transfer and it only accumulates the electric charge as potential is applied.⁸⁰ This behavior is due to the high surface area and high conductivity of MWCNT, which improves



Figure 4.6: Electrochemical potential window over GCE in 0.5 M NaNO₃ from -1.8 to 2 V for three different composites at 25 mV s^{-1}

the capacitance of the polymer. However, from the charge-discharge experiment, an accurate value of capacitance can be obtained.⁸¹



Figure 4.7: (a) CV for fCNTs/PANI/GCE which shows two redox couple: A_1/B_1 and A_2/B_2 . (b) CV for three different composites at 25 mV s⁻¹ 5 mM K₃ [Fe(CN)₆] in 0.5 M NaNO₃ under room temperature. fCNTs/PANI/GCE shows the largest area which is related to the high capacity of the system.

In Fig.4.7 (a), fCNTs/PANI/GCE composite electrode shows two electron couples of redox reactions in CV plot, A_1/B_1 and A_2/B_2 . A_1/B_1 which corresponds to the redox transition from leucoemeraldine, the semiconducting state of PANI, to polaronic emeraldine form, which is the conducting state of PANI. On the other hand, A_2/B_2 is attributed to the transformation from emeraldine to pernigraniline.⁷⁹

4.2.2 Evaluation of redox reversibility

This section shows a CV study for each electrode based on the variation of the scan rates from 5 to 100 mV s^{-1} in an electrolytic solution of potassium ferricyanide. At first, the Randles-Sevcik equation was used to study the reversibility of the system, the determination of the mechanism of mass transfer reaction and the calculation of the diffusion coefficients for each composite. Then, the standard heterogeneous rate

constant was calculated based on the Nicholson-Kochi treatment. In the end, this section demonstrates which composite has the greatest k^0 and a respective interpretation regarding photocatalytic activity.

PANI

Fig. 4.8 shows the evolution of voltammograms of oxidative-polymerized PANI/GCE under (1) illuminated, (2) dark and (3) UV conditions. CV shows well-defined redox peaks for the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ couple at 0.17 V and 0.29 V, respectively. Under illuminated and dark conditions (Fig. 4.8 1 and 2 (a) plots), there is a peak that appears at -0.2 V visible for all the scan rates (low and high scan rates). As was mentioned before, these peaks correspond to the oxidation of the polaronic emeraldine form of PANI.⁷⁹ By UV-Vis results is alredy known that ES PANI absorbs at 503 and 650 nm, and our lamp emits at 365 nm. Therefore, under UV radiation, this peak does not appear because the lamp wavelength emission does not promote the redox transition.

From the peak-to-peak difference, the Randles-Sevcik plot is also shown in Fig. 4.8 part b. In all the plots, the linear relationship persists for the anodic and cathodic peak currents, suggesting that the composite follows a diffusion-controlled reaction.⁸² Under UV radiation, PANI/GCE exhibits the best correlation coefficients ($R_a = 0.993$ and $R_c = 0.996$). For the whole system, little deviations from linearity imply a quasi-reversible system, because Randles-Sevcik equation is given for a reversible redox reaction. Another point to take into consideration is the peak-to-peak separation. When the difference between peak potential shifts with the scan rate, a quasi-reversible process is in development.³⁵

For a better understanding of the of quasi-reversibility, a linear plot of ΔE_p vs log ν is studied (Fig. 4.9 part c). Both in illuminated and dark conditions shows a R = 0.969 indicating a reversible reaction in contrast with UV conditions which shows a deviation from linearity with an R = 0.837.

The main difference between the three cases is due to the variation in current response depending on



Figure 4.8: (a) Cyclic voltammetric response, (b) Randles-Sevcik plot and (c) quasi reversible study of PANI/GCE obtained for 5 mM K₃ [Fe(CN)₆] in 0.5 M NaNO₃ with scan rates of 100, 50, 25, 15, 10 and 5 mV s⁻¹ in different environments: 1) illuminated, 2) dark, and 3) UV.

the environment that PANI/GCE is exposed to. At the scan rate of 100 mV s^{-1} under UV, the current response (i_{UV}) is 350 µA in contrast with light (i_L) and dark (i_D) with 52 and 36 µA, respectively. It shows an increase in current under UV radiation $(i_D < i_L < i_{UV})$. This current that passes through the electrode is limited by the diffusion of the species that are directed to the electrode surface. By changing the cell's potential, the concentration of the species on the electrode surface also changes. With higher scan rates, the diffusion layer thickness decreases, causing higher concentrations of redox near the electrode, resulting in higher currents.

fCNTs/PANI/GCE composite

Chemical functionalization of carbon nanotubes has been done to increase the interfacial binding between CNTs and PANI.⁸³ The same CV study was performed with this composite. Fig. 4.9 shows the voltammograms for the fCNTs/PANI composite for (1) illuminated, (2) dark and (3) UV conditions. Four peaks corresponding to two redox couples are found in the voltammogram under illuminated and UV conditions. It infers that peaks at +0.61 V and +0.42 V at 50 mV s⁻¹ are consistent with PANI redox reaction and peaks at +0.28 V and +0.18 V match de ferricyanide redox couple. However, in the dark, there is just the redox peak of ferricyanide.

It is notable that for these CVs, capacitive currents are higher, giving the voltammograms a broader appeareance, in comparison to pure PANI/GCE. It indicates that there is greater non-faradaic current in the system. This is due to the high porosity that the nanotubes give to the polymer. This porosity means that there are more active sites in the composite, increasing its charge distribution, making it a good capacitor. The peaks that do not correspond to the redox reaction of ferricyanide but are attributed to the charge transfer of the quinones and benzoquinones of the PANI and to the co-existence of several types of functional groups present in the nanotubes.⁸⁴



Figure 4.9: (a) cyclic voltammetric response, (b) Randles-Sevcik plot and (c) quasi reversible study of fCNTs/PANI/GCE obtained for 5 mM K₃ [Fe(CN)₆] in 0.5 M NaNO₃ with scan rates of 100, 50, 25, 15, 10 and 5 mV s⁻¹ in different environments: 1) illuminated, 2) dark, and 3) UV.

In Randles-Sevcik plots (Fig. 4.9(b)), linear behavior can be observed as in the case of PANI/GCE, with an average correlation coefficient of 0.991, which also indicates a controlled diffusion process. In the plots of ΔE_p vs logv (Fig. 4.9 part c), the three cases present non-linear behaviors that cannot confirm a quasi-reversible reaction of the ferricyanide with the electrode. To achieve a conclusion, another criterion is applied like the range of Ψ values. In Table B.2 are listed in detail the Ψ values, which are less than one. It confirms that system is quasi-reversible. Once again, the main difference between the three cases is due to the variation in current response depending on the environment that fCNTs/PANI/GCE is exposed to. At the scan rate of 100 mV s⁻¹ under dark conditions, the current response (iD) is 1309 μ A in contrast with light (i_L) and UV (i_D) with 1280 and 958 μ A, respectively. It shows an increase in current under dark conditions (i_{UV} <i_L <i_D).

CNTs-TiO₂/PANI/GCE composite

To continue improving the advantage of fCNTs/PANI/GCE composite, this hybrid material is dopped with an inorganic nanocluster resulting in a new composite. This study was interested in TiO₂ because of its high UV-sensitivity,⁸⁵ strong oxidizing power, long-term stability, and photostability.⁸⁶.

In CV study, the voltammograms for this composite show curves that are not as broad as the fC-NTs/PANI/GCE composite. This is mainly due to the interaction between TiO₂ nanoparticles with the carboxyl groups of the nanotubes, and with the rings of the polymer, causing a reduction in its surface area, suggesting a decrease in the capacity to store energy. This implication is consistent with the BET analysis for fCNTs and TiO₂, with a specific surface area of (298.40 ± 2.72) m² g⁻¹ and (147.02 ± 1.89) m² g⁻¹, respectively.⁸⁷

In Randles-Sevcik plots (Fig. 4.10(b)), linear relationship pattern is observed as in the case of PANI/GCE and fCNTs/PANI/GCE composites, with an average correlation coefficient of 0.986, which also indicates a diffusion controlled process. In the plots of ΔE_p vs log v (Fig. 4.10 part c), the 3 conditions



Figure 4.10: (a) cyclic voltammetric response, (b) Randles-Sevcik plot of peak current vs square root of scan rate and (c) quasi reversible study of CNTs-TiO₂/PANI/GCE obtained for 5 mM K₃ [Fe(CN)₆] in 0.5 M NaNO₃ with scan rates of 100, 50, 25, 15, 10 and 5 mV s⁻¹ in different environments:1) illuminated, 2) dark, and 3) UV.

present non-linear behaviors that do not confirm a quasi-reversible reaction of the ferricyanide with the electrode. To achieve a conclusion, another criterion is applied like the range of Ψ values. In Table B.2 are the whole values of Ψ , which are less than one, under illuminated, dark and UV. This infers that the system is quasi-reversible. Once again, the main difference between the three cases is due to the variation in current response depending on the environment that fCNTs/PANI/GCE is exposed to. At the scan rate of 100 mV s⁻¹ under UV, the current response (i_{UV}) is 183 µA in contrast with light (i_L) and dark (i_D) with 113 and 99 µA, respectively. It shows an increase in current under UV radiation (i_D <i_L <i_{UV}).

4.2.3 Diffusion Coefficients and kinetic parameters

The Randles-Sevcik equation was also used to determine the diffusion coefficient of every system. Values between $(2.2 \pm 0.7) \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ and $(4.0 \pm 2.7) \times 10^4 \text{ cm}^2 \text{ s}^{-1}$ were obtained for UV experimental data. The value for *D* given in literature is $(7.3 \pm 0.7) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.⁸⁸ A possible sources of error can be related to reduction of the effective surface area of the electrode.⁸⁹ Obtained experimental data is reported in Table 4.2.

For a simple quasi-reversible electrochemical reaction, the kinetic parameter Ψ is calculated by also performing CV experiments with the diffusion coefficient data obtained from Randles-Sevcik calculation. As outlined above, Ψ is used to determine the heterogeneous standard rate constant k^0 of electron transfer reaction. Nicholson-Kochi treatment was carried out for every composite.

CNTs-TiO₂/PANI/GCE and PANI/GCE composites exhibit a difference of peak potentials ΔEp (anodic and cathodic) > 60 mV s⁻¹, and fCNTs/PANI/GCE composite showed a $\Delta Ep < 60$ mV s⁻¹. Considering an extensive ΔEp range, Eq.3.4 is used for calculation of Ψ . Dimensionless parameter Ψ also denotes electrochemical reversibility, when $\Psi \leq 7$ the system is defined as quasi-reversible⁶². According to that criterion, Ψ varies from 0.1 to 0.7 for PANI/GCE, from 0.1 to 4 for fCNTs/PANI/GCE, and from 0.3 to

1.1 for CNTs-TiO₂/PANI/GCE composites under UV irradiation. This suggest that all composites have quasi-reversible behavior. Detailed calculations of k^0 and Ψ are given in Appendix B.

Illuminated			
Electrode	$D [\mathrm{cm}^2 \mathrm{s}^{-1}]$	k^{0} [cm s ⁻¹]	quasi-reversibility
PANI/GCE	$(2.2 \pm 0.7) \ge 10^{-6}$	$(2.7 \pm 0.1)x10^{-5}$	yes
fCNTs/PANI/GCE	$(6.1 \pm 4.1) \ge 10^{-4}$	$(7.2 \pm 2.8)x10^{-5}$	yes
CNTs-TiO ₂ /PANI/GCE	$(1.3 \pm 0.2) \ge 10^{-5}$	$(5.3 \pm 0.3)x10^{-5}$	yes
Dark			
Composite	$D [\mathrm{cm}^2 \mathrm{s}^{-1}]$	k^{0} [cm s ⁻¹]	quasi-reversibility
PANI/GCE	$(1.1 \pm 0.4) \ge 10^{-6}$	$(8.1 \pm 1.5)x10^{-6}$	yes
fCNTs/PANI/GCE	$(4.0 \pm 2.7) \ge 10^{-4}$	$(8.5 \pm 2.9)x10^{-5}$	yes
CNTs-TiO ₂ /PANI/GCE	$(1.1 \pm 0.2) \ge 10^{-5}$	$(7.9 \pm 2.1)x10^{-6}$	yes
UV			
Composite	$D [\rm cm^2 s^{-1}]$	k^{0} [cm s ⁻¹]	quasi-reversibility
PANI/GCE	$(6.5 \pm 3.0) \ge 10^{-5}$	$(1.5 \pm 0.2)x10^{-4}$	yes
fCNTs/PANI/GCE	$(6.6 \pm 4.5) \ge 10^{-4}$	$(6.8 \pm 3.9)x10^{-5}$	yes
CNTs-TiO ₂ /PANI/GCE	$(1.5 \pm 0.6) \ge 10^{-5}$	$(6.6 \pm 1.6)x10^{-5}$	yes

Table 4.2: Summary of the diffusion coefficients D standard heterogeneous rate constant k^0 and quasi-reversibility study for each composite.

Finally, k^0 is obtained from the slope of Ψ vs $v^{-1/2}$ plot, according to the Eq. 3.2. These values are reported in Table 4.2. For the PANI/GCE, the increase in the standard rate constant is evident because its values change in one order of magnitude. Darkness is the least favored condition against daylight and UV irradiation, with a k^0 value of $(8.1 \pm 1.5) \times 10^{-6} \text{ cm s}^{-1}$. Then, under daylight environment, the kinetic of the system increases with a k^0 value of $(2.7 \pm 0.1) \times 10^{-5} \text{ cm s}^{-1}$. Finally, when the electrochemical cell is irradiated with UV light, it shows a k^0 value of $(1.5 \pm 0.2) \times 10^{-4} \text{ cm s}^{-1}$ being the highest value of all the systems under study.

For the fCNT/PANI/GCE, all its k^0 values are similar, as under dark, with a k^0 of $(8.5 \pm 2.9) \times 10^{-5}$ cm s⁻¹; illuminated, with a k^0 of $(6.1 \pm 4.1) \times 10^{-4}$, and UV conditions with a k^0 of $(6.6 \pm 4.5) \times 10^{-4}$. This implies that there is no major difference in the rate of electron transfer of the redox reaction. In general, the polymer and the functionalized carbon nanotubes structures do not require natural light or UV irradiation to initiate a catalysis reaction. For that reason, under the same conditions, the electron transfer can be achieved. However, in this composite the values of k^0 decrease against the PANI/GCE composite due to its new interaction of the free electrons of PANI rings with the functional groups of carbon nanotuves, that in the same time, these contribute to increase of their non-faradaic current.

For the CNTs-TiO₂/PANI/GCE electrode under dark conditions, the k^0 shows a value of (7.9 ± 2.1) x 10^{-6} cm s⁻¹, increasing one order of magnitude under daylight with a value of (5.3 ± 0.3) x 10^{-5} cm s⁻¹. Finally the rate changes slightly when the electrode is exposed to UV irradiation with a k^0 value of (6.6 ± 1.6) x 10^{-5} cm s⁻¹. This indicates that the charge transfer is faster under illuminated and UV conditions. Actually, this is due to activation of TiO₂ nanoparticles under UV irradiation. On the contrary, under dark conditions there is no promotion of electrons in the inorganic cluster of titania that could help to accelerate this charge transfer. However, it was expected that the composite electrode containing TiO₂ would present the highest rate constant. A possible explanation for the underperformance of the CNTs-TiO₂/PANI/GCE composites in comparison to the pure PANI/GCE could be due to the low amount of TiO₂ NPs in the carbon nanotubes and hence in the polymer matrix. Also, the tendency of titania to agglomerate due to its high surface energy, could be an explanation. Nevertheless, in terms of speed of electron transfer between an electroactive species and an electrode surface, PANI/GCE performs the best out of the three composites, due to its high conductive properties.⁶²

However, it was expected that doping with $CNTs-TiO_2$ would increase the current response. This result aside, the principal objective is the photodegradation of organic pollutants. This photodegradation starts with oxidizing species that titania can create under UV illumination, which can help to further break the

bonds within the pollutant molecules to further aid with degradation. The mechanism proposed for the formation of reactive species is defined as follows⁹⁰:

$$TiO_2 + h\nu \rightarrow TiO_2 + e^- + h^-$$
$$O_2 + e^- \rightarrow O_2^{\bullet -}$$
$$H_2O + h^+ \rightarrow OH^{\bullet} + H^+$$
$$OH^- + h^+ \rightarrow OH^{\bullet}$$

Reaction occurs on the surface of Titania.⁹⁰ Under UV illumination, electron-hole pairs are created on its surface and oxidants $O_2^{\bullet-}$ and OH^{\bullet} are generated, being strong enough to oxidize organic contaminants.⁹¹

Comparison between different environments for the composites



Figure 4.11: Comparison between three different environments: illuminated, dark and UV for (a) PANI/GCE, (b) fCTNs/PANI/GCE, and (c) CNTs-TiO₂/PANI/GCE at 25 mV s⁻¹

In Fig. 4.11 (a) for PANI/GCE, is evident that the current has increased from dark to UV conditions in 19.4 μ A. In Fig. 4.11 (b) for fCNTs/PANI/GCE, exists a remarkable increment in the current of 593 μ A, and also due to the broad peaks in the voltammogram, is confirmed the capacitive behavior of this

electrode. Finally, from comparison of the area surrounded by the curves in Fig. 4.11 (c), the current of the CNTs-TiO₂/PANI/GCE composite has increased in 82 μ A when it is irradiated by UV light. The presence of some oxide groups and TiO₂ nanoparticles on the surface of CNTs played a key role on inducing redox reactions and contributing to the part of the pseudo capacitance.⁹² Undoubtedly, the UV light irradiation enhanced in an effective way the electrochemical properties of the composites electrode, being consistent with the results from the cyclic voltammetry experiments.

4.3 Electrochemical impedance spectroscopy

Nyquist and Bode plots for PANI/GCE, fCNTs/PANI/GCE and CNTs-TiO₂/PANI/GCE were plotted and analyzed. As described earlier, R_{CT} represents the charge transfer resistance and is a measure for the facility of a redox reaction to occur at the electrode, hence it is expected that a system with a higher k^0 also presents a lower R_{CT} . As a result, equivalent circuits for all composites were modeled and compared to the Nyquist and Bode plots in order to obtain the R_{CT} values.

PANI

Fig. 4.13 shows Nyquist and Bode plots of PANI/GCE composite. Its fitting curve is constructed from its equivalent circuit, which is shown in Fig. 4.12. Estimated values for R_{CT} are obtained from the fit. Due to the composite's porosity and non-uniform morphology, a Randles circuit was modified by a CPE element. The obtained parameters from the fitting curve are reported in Table 4.3.

At low frequencies in the Nyquist plot (Fig. 4.17 (a)), a semicircle is observed suggesting a dominant charge transfer resistance. This resistance increases under dark conditions, and decreases when the electrochemical cell is exposed to UV and natural light irradiation. At high frequencies, a straight line with a slope of 0.5 suggests a diffusion process which is accounted for in the circuit by a Warbug resistance. Under dark conditions, this line deviates from the Φ -axis with phase angle close to 50° on the Bode plot



Figure 4.12: Modified Randles circuit for the fitting of Nyquist and Bode plots for PANI/GCE composite.

	UV		illuminated		Dark	
Element	Value	Error(%)x 10 ⁻⁵	Value	Error(%)x 10 ⁻⁵	Value	Error(%) x 10 ⁻⁵
R_S/Ω	101.93	7.63	48.7	7.63	38.9	7.63
R_{CT}/Ω	246.16	7.63	198.5	7.63	354.5	7.63
W_1/Ω	558.14	7.63	471.5	7.63	1524.7	7.63
CPE/F	$1.7x10^{-5}$	7.63	$1.x10^{-6}$	7.63	$2.1x10^{-5}$	7.63
n_1	0.98	7.63	0.97	7.63	0.98	7.63

Table 4.3: Equivalent circuit parameters for PANI/GCE composite.

(Fig. 4.17(b)) for the phase angle as a function of the frequency. The presence of one peak on the Bode plot denotes that it has one apparent time constant present in the system. This demonstrate that the choice of the proposed circuit is also correct.

Moreover, the capacitance is obtained from the fitting curve of the equivalent circuit. This capacitance decreases from dark, with a value of 2.1×10^{-5} F, to UV with a value of 1×10^{-6} F. From these results, the best capacitive behavior is shown for PANI/GCE under dark conditions.

From the plot of the real impedance as a function of frequency, there are two peaks presence at lower and higher frequencies. Both peaks are similar to the ones reported earlier, which may be due to the microphase separation of the polymer chains.⁹³ In this plot is evident that there is no a large difference between the Z values of illuminated and UV conditions. However, from the equivalent circuit parameters, the R_{CT} falls from dark, to UV and finally to illuminated conditions, with values of 354.5 Ω , 246.16 Ω ,



Figure 4.13: (a) Nyquist plot and (b) Bode plot for the PANI/GCE composite under three different environments.

	Parameters		
Conditions	$R_{CT}[\Omega]$	k^{θ} [cm s ⁻¹]	
Dark	354.5	$(8.1 \pm 1.5) \ge 10^{-6}$	
Illuminated	198.5	$(2.7 \pm 0.1) \ge 10^{-5}$	
UV	246.2	$(1.5 \pm 0.2) \ge 10^{-4}$	

and 198.5 Ω , respectively.

Table 4.4: Comparison between R_{CT} and k^0 of PANI/GCE composite under three different environments.

According to the values obtained for k^0 , a lower charge transfer resistance is expected for the system with the highest rate constant. Consequently, R_{CT} should be lower under UV, followed by natural light and lastly the systems under dark conditions, unlike the results presented in Table 4.4. A possible explanation can be that the composition and morphology of the composite over the electrode, which is not the same over the whole experiments, resulted in slight differences on the EIS experiments.
4.3.1 fCNTs/PANI/GCE composite

Fig. 4.15 shows the Nyquist and Bode plots of fCNTs/PANI/GCE. Its fitting curve is constructed from its equivalent circuit, which is shown in Fig. 4.14. Estimated values for R_{CT} are obtained from its fitting plot.



Figure 4.14: Modified Randles circuit for the fitting curves of Nyquist and Bode plots for fCNTs/PANI/GCE composite.

The difference with the PANI/GCE equivalent circuit is based on the use of a capacitor, suggesting that the surface of this composite is more uniform and well dispersed than PANI/GCE, making the use of a CPE unnecessary. Parameters of the fitting curves are reported in Table 4.5.

	UV		illuminated		Dark	
Element	Value	Error(%)x 10 ⁻⁵	Value	Error(%)x 10 ⁻⁵	Value	Error(%) x10 ⁻⁵
R_S/Ω	$2.2x10^{-5}$	-	$2.2x10^{-13}$	-	$6.3x10^{-13}$	-
R_{CT}/Ω	31.7	1.94	54.9	0.05	54.9	0.05
W_1/Ω	65.6	3.14	172.6	0.09	172.6	0.08
C_{DL}/F	$3.3x10^{-8}$	13.98	$2.2x10^{-9}$	1.92	$2.5x10^{-9}$	1.92

Table 4.5: Equivalent circuit parameters for fCNTs/PANI/GCE composite.

Fig.4.15 (a) shows the Nyquist plot of fCNTs/PANI/GCE. At low frequencies, part of a semicircle is observed suggesting a charge transfer resistance. At higher frequencies, a straight line with a slope of 0.5 implies a diffusion process which is denoted by the Warbug resistance. From the Nyquist plot fitted

spectrum is evident that it is not possible to fit the semicircle. In consequence, R_S fitted values are very small, and the errors associated to it are very large that can be neglected. These values are reported in Table 4.5.

From the Bode plot at higher frequencies, there is no noticeable changes in the real impedance. On the other hand, at lower frequencies, the composite under illuminated and dark conditions present a phase angle of 37°. This value decreases under UV irradiation, suggesting a higher capacitive behaviour in contrast with the other environmental conditions of the experiment. Indeed, the capacitance values from



Figure 4.15: (a) Nyquist plot and (b) Bode plot for the fCNTs/PANI/GCE composite under three different environments.

the equivalent circuit proposed increases when the fCNTs/PANI/GCE is exposed from illuminated to UV irradiation conditions, with a C = 3.3×10^{-8} F. For the illuminated and dark conditions, the capacitance values are 2.2 and 2.5 x 10^{-9} F, which are similar to each other. From these results, the best capacitive behavior is shown for fCNTs/PANI/GCE under UV irradiation.

The values of R_{CT} versus k^0 are in good agreement, with a slight deviation for the sytem under UV

irradiation, as it shown in Table 4.8. As it is mentioned before, the values of k^0 are very close to each other, and slight changes in the experiment could alter the system, and could lead to the false conclusion that one experimental condition creates more favorable results, as in this study, photocatalytic potentials, over others. Having mentioned that, the EIS experiment slightly infers a faster for the electrode that is exposed to UV radiation.

	Parameters		
Conditions	$R_{CT}[\Omega]$	k^{θ} [cm s ⁻¹]	
Dark	54.9	$(8.5 \pm 2.9) \ge 10^{-5}$	
Illuminated	54.9	$(7.2 \pm 2.8) \ge 10^{-5}$	
UV	31.7	$(6.8 \pm 3.9) \ge 10^{-5}$	

Table 4.6: Comparison between R_{CT} and k^0 of fCNTs/PANI/GCE composite under three different environments.

4.3.2 CNTs-TiO₂/PANI/GCE composite

Fig.4.17 shows Nyquist and Bode plots of CNTs-TiO₂/PANI/GCE composite. Its fitting curve is constructed from its equivalent circuit, which is shown in Fig. 4.16. Estimated values for R_{CT} are obtained from the fit, and this parameters are reported in Table 4.7.



Figure 4.16: Modified Randles circuit for the fitting of Nyquist and Bode plots for CNTs-TiO₂/PANI/GCE composite.

Fig. 4.17(a) shows the Nyquis plot of CNTs-TiO₂/PANI/GCE composite. At low and high frequencies,

	UV		Illuminated		Dark	
Element	Value	Error(%)x10 ⁻⁵	Value	Error(%)x10 ⁻⁵	Value	Error(%) x10 ⁻⁵
R_S/Ω	43.5	7.63	44.5	7.63	45.4	7.63
R_{CT}/Ω	1001.7	7.63	1634	7.63	1711.3	7.63
W_1/Ω	9517.8	7.63	13179	7.63	13192	7.63
CPE_1/F	$5.9x10^{-5}$	7.63	$1.5x10^{-5}$	7.63	$1.5x10^{-5}$	7.63
<i>n</i> ₁	0.645	7.63	0.785	7.63	0.789	7.63

Table 4.7: Equivalent circuit parameters for CNTs-TiO₂/PANI/GCE composite.

a straight line pattern is associated to the good conductivity of the whole composite due to the doping with TiO_2 .⁹⁴ There is no observable semicircle present in the plot, so a dominant diffusion contribution is suggested. Furthermore, a Bode plote is necessary to infer more information about the composite behavior.

At low frequencies, CNTs-TiO₂/PANI/GCE exhibits capacitive behavior. Almost a vertical line should be observed on Nyquist plot. Instead of that, it deviates from Φ -axis with phase angle close to 60° on the Bode plot (Fig.4.17 (b)) for the phase angle as a function of the frequency. This behavior is due to pseudocapacitance effects from oxygen groups of TiO₂. Therefore, a capacitor (C_{DL}) would not fit a good electrical equivalent circuit, so it is replaced by another capacitive element such as CPE.

From the fitting curve, capacitance is also estimated. In general, the capacitance values only show a slight change for the conditions under UV irradiation. It varies from dark ($1.0 \ 10^{-5}$ F), to natural light ($1.5 \ x \ 10^{-5}$ F) and to UV conditions ($5.9 \ x \ 10^{-5}$ F). Despite this, there is a slight variation of capacitance from dark to UV. These values remain almost the same due to the insertion of TiO₂ at the composite which lowers the capacitance of the whole electrode at different environments.⁹⁴ This behavior agrees with the cyclic voltammetry study, where the current values of dark and UV conditions are 134 μ A and 216 μ A, respectively. From these results, the best capacitive behavior is shown for CNTs-TiO₂/PANI/GCE under UV irradiation.



Figure 4.17: (a) Nyquist plot and (b) Bode plot for the CNTs-TiO₂/PANI/GCE composite under three different environments.

In effect, the R_{CT} values falls from dark to illuminated, and UV conditions, with 1711.3 Ω , 1634.0 Ω , and 1001.7 Ω , respectively; while k^0 increases from dark to UV conditions according with the cyclic voltammetry study, as shown in Table 4.8.

	Parameters		
Conditions	$R_{CT}[\Omega]$	k^{θ} [cm s ⁻¹]	
Dark	1711.3	7.9 x 10 ⁻⁶	
Illuminated	1634.0	5.3 x 10 ⁻⁵	
UV	1001.7	6.6 x 10 ⁻⁵	

Table 4.8: Comparison between R_{CT} and k^0 of CNTs-TiO₂/PANI/GCE composite under three different environments.

Chapter 5

Conclusions & Outlook

The principal objective of this work was to design electrodes based on polyaniline doped with functionalized carbon nanotubes and also carbon nanotubes doped with TiO₂ nanoparticles for the improvement of the photocatalytic activity of the composites. This study contrasted the PANI/GCE performance over the fCNTs/PANI/GCE and CNTs-TiO₂/PANI/GCE in order to determine kinetic parameters and charge transfer resistance under daylight, dark and UV conditions with further application in photodegradation of organic pollutants. In this manner, the electrode with the highest k^0 and lowest R_{CT} will be suitable for the catalytic process. This is the case for the PANI/GCE. However, CNTs-TiO₂/PANI/GCE can also undergo photodegradation due to the TiO₂ NPs in the matrix.

From the UV-Vis study, the oxidative polymerization synthesis of polyaniline in the emeraldine salt oxidation state was confirmed by the peaks at 290 nm and 503 nm due to the π - π transition and polaron- π transition, respectively. Furthermore, signals in the FT-IR spectrum verify the N-H stretching at 2910 and 2997 cm⁻¹, and the C=C phenyl ring stretching at 1663 cm⁻¹, proving the right synthesis of the polymer.

From physical characterization with TEM, it was confirmed the presence of TiO_2 nanoparticles along the carbon nanotubes walls. With the use of XRD technique, the diffractogram of TiO_2 supported the synthesis of TiO_2 in its anatase crystalline phase. By the Scherrer equation, the average particle size of TiO_2 obtained is 8 nm. Finally, the FT-IR spectrum of TiO_2 validated the formation of Ti-O/Ti-O-Ti bonds at 580, 600 cm⁻¹.

The synthesis of the composites was also supported by UV-Vis. For the fCNTs/PANI/GCE, is confirmed the interaction of the nanotubes over the PANI matrix by the peak present at 268 nm. And for the CNTs-TiO₂/PANI/GCE, the peak at 280 nm appears due to the surface plasmon resonance of TiO₂ over the polymer. At the end, the FT-IR study proved the effective synthesis of the composites since their spectrum share the same peaks with the fCNTs, TiO₂ and polyaniline.

From the cyclic voltammetric response, the anodic and cathodic peak currents for the calculation of the diffusion coefficient by Randles-Sevcik equation are obtained. This *D* values are in the range of (2.2 ± 0.7) x 10^{-7} cm² s⁻¹ and (4.0 ± 2.7) x 10^4 cm² s⁻¹ that were obtained for UV experimental data. Whole systems showed a linear response with Pearson's coefficients above the 0.990, indicating a diffusion controlled process. Moreover, the analysis of reversibility was performed by the ΔEp vs log *v* plot and the study of Ψ , confirming that all the composites are quasi-reversible systems.

From the Nicholson-Kochi treatment and EIS, PANI/GCE is the composite with the highest k^0 with a value of $(1.5 \pm 0.2) \ge 10^{-4}$ cm s⁻¹, and R_{CT} equals to 246.2 Ω , under UV irradiation. However, it was expected that the composite electrode containing TiO₂ would present the highest rate constant, which is explained by the low effective concentration of TiO₂ Nps in the matrix. Furthermore, it is noticeable to mention that titania has the tendency to agglomerate due to its high surface energy. Therefore, the most suitable electrode to achieve the photocatalytic activity with further degradation of pollutants is the the CNTs-TiO₂/PANI/GCE with a k^0 of $(6.6 \pm 1.6) \ge 10^{-5}$ cm s⁻¹, and a $R_{CT} = 1001.7 \Omega$.

This result infers that the less favored composite is the one with the functionalized carbon nanotubes. This is due to its higher capacitance behavior demonstrated by their broad peaks in cyclic voltammetry with a current value of 1420 μ A in contrast with the PANI/GCE and the CNTs-TiO₂/PANI/GCE with current values of 22.1 and 216 μ A, at 25 mV s⁻¹ under UV irradiation. However, by EIS study through the equivalent circuits adapted for each composite suggests the CNTs-TiO₂/PANI/GCE has higher capacitive with a C = 5.9 x 10⁻⁵ F, in contrast with the fCNTs/PANI/GCE and the PANI/GCE, with C = 3.3 x 10⁻⁸ F and C = 1.7 x 10⁻⁵ F, respectively.

To conclude, it is suggested that the composites based on PANI/GCE and CNTs-TiO₂/PANI/GCE should be studied in regard to their ability to degrade organic pollutants.

Appendix A

FT-IR of TiO₂ nanoparticles



Figure A.1: FT-IR spectrum of TiO₂ nanoparticles prepared at 500°C

Appendix B

Kinetic parameters

Electrode	illuminated	Dark	UV
PANI/GCE	55.26	89.57	11.22
fCNTs/PANI/GCE	4.51	3.52	3.65
CNTs-TiO ₂ /PANI/GCE	24.84	27.87	23.42

On this chapter, the kinetic parameters obtained from Nicholson-Kochi method are listed in detail.

Table B.1: Dimensionless Nicholson-Kochi factor obtained from CV experiments using equation. 3.3

PANI/GCE					
Illuminated	Dark	UV			
0.960	0.739	0.563			
1.057	1.208	1.095			
1.096	1.272	0.739			
1.208	1.610	0.715			
1.272	1.723	0.631			
1.422	2.174	0.483			
fCNTs/PANI/GCE					
Illuminated	Dark	UV			
0.369	0.423	0.399			
0.461	0.497	0.495			
0.497	0.544	0.545			
0.501	0.571	0.545			
0.507	0.574	0.538			
CNTs-TiO/PANI/GCE					
Illuminated	Dark	UV			
0.439	0.363	0.100			
0.548	0.377	0.209			
0.563	0.402	0.377			
0.631	0.420	0.483			
0.821	0.449	0.548			
-	0.631	0.715			

Table B.2: Summary of the dimensionless kinetic parameter Ψ for each composite under different environments



Figure B.1: Nicholson-Kochi treatment for the evaluation of heterogeneous standard rate constant k^0 of electron transfer from CV data. From left to right: Plot of Ψ vs $v^{-1/2}$ and Plot of Ψ values vs ΔEp for the reduction of 5 mM K₃ [Fe(CN)₆] in 0.5M NaNO₃ at CNTs-TiO₂/PANI/GCE.

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