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Innovation in the Electrophoretic Deposition of TiO₂ Using Different Stabilizing Agents and Zeta Potential

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Abstract

Surface engineering is gaining increasing relevance in various industrial sectors and in research, and in this sense, zeta potential measurements, being a physicochemical parameter of interface, are key to linking the functionality of a coating with its application environment. In this work, different stabilizing agents with different chemical structure and electrical charge were used to improve the stability of the TiO₂ particles. The influence of the electrophoretic deposition (EPD) parameters (potential and deposition time) and the concentration of chitosan and TiO₂ in suspension were studied to find the best deposition performance on the titanium substrate. The composition and structure of the coatings were evaluated by infrared spectroscopies (FT-IR) and scanning electron microscopy (SEM). It was observed that the TiO₂ particles were dispersed in the chitosan matrix through simultaneous deposition. Corrosion resistance was evaluated by electrochemical polarization curves, indicating a higher corrosion resistance of TiO₂ and TiO₂-chitosan coatings compared to the pure titanium substrate in a solution of sulfuric acid.

Keywords: electrophoretic deposition, zeta potential, chitosan, TiO₂

1. Introduction

Nowadays, surface engineering is of great scientific and technological relevance focused on the development of new methods to achieve desired surface properties and provide better performance of materials.

The methods of surface modification are used to develop a wide range of functional properties including physical, chemical, biological, electrical, electronic, magnetic, adhesion, mechanical, wear-resistant, and corrosion-resistant properties on the required substrate surfaces.

The industrial sectors that demand the development and application of the surface modification of materials are the automotive, aerospace, missile, energy, electronics, biomedical, textile, petroleum, petrochemical, chemical, steel, energy, cement, machine tool, and construction industries [1].

There are different methods that allow the coating of a surface, to mention some, such as painting, carburizing, nitriding, sputtering, electrophoretic deposition, spray coatings, electrodeposition, ion implantation, ion plating, thermal oxidation, laser cladding, electroless deposition, chemical vapor deposition, solvent casting, dip coating, and sol-gel coating [2].

Within the variety of coating methods, the electrophoretic deposition (EPD) has several advantages, such as low deposition time, simple and cheap equipment, little restriction of the shape of substrates; deposition is achieved both inside of the cavities and on the outside cavity surfaces, control the film thickness and uniformity, applicability to any powdered solid that forms a stable, a wide range of particle sizes, from micro- to nanometric particles (colloidal suspensions) [3].

Almost all types of substrates, including metal oxides, ceramics, polymers, and composite materials, can be coated by EPD with similar or different materials.

Using EPD, the coating of different substrates has been made with a variety of materials, to mention a few, metals, polymers, ceramics, glasses, carbon nanotubes, nanoparticles, zeolite, hydroxyapatite, silica, alumina, proteins, bacteria, and cells [4–8].

Moreover, considering the functionality and application the films can be used in antioxidant coatings, bioactive coating, cell fuel, tissue engineering, composites, medical implants, scaffolds, microelectronic devices, wear-resistant, sensors, nanoscale assembly, luminescent materials, gas diffusion electrode, biomedical, multilayer composites, bactericide surfaces, piezoelectric motors, photocatalyst and photovoltaics, corrosion protective, and water purification [9–22].

EPD is based on the movement of charged particles suspended in a solution through application of an external electric field (electrophoresis mechanism). This electric field enables the consolidation of particles into films, cast onto any shaped substrate, or into thick and bulk components.

The electrophoretic deposition process is generally described in three stages: the first consists in the application of an electric field between an anode and a cathode, which are submerged in the suspension of the charged particles, which causes the migration of the charged particles toward the opposite charged electrode. Subsequently, the particles begin to accumulate on the surface of the electrode resulting in the formation of a thin and thick film. Finally, a thermal treatment step is carried out to improve the characteristics of electrodeposits [1, 2].

To employ electrophoretic deposition successfully, a basic understanding of the colloidal stability, the deposition kinetics, and the constrained drying and sintering issues of the deposit is necessary.

Although the EPD technique is simple, it is necessary to understand the coupled electrical and physicochemical phenomena of the particles that are initially suspended, and at the end

of the process, are adhered to a surface. For this purpose, it is advisable to analyze the physicochemical environment to which a suspended particle is subjected, either dispersed or in the colloidal phase. One of the best known models for studying the colloidal phase or the stability of suspended particles is the double electrical layer (DEL), which consists of recognizing the distribution of electric charges around a particle surrounded by solvent molecules and counter ions that define its solid–liquid interface [2–4].

The zeta potential (ζ) is an electrochemical parameter that allows estimating the nature of the surface charge of the suspended particles, establishing whether the electrophoretic deposition process is anodic or cathodic and deposition kinetic. For example, if we compare a $\zeta = 100$ mV with a $\zeta = 10$ mV, the electrophoretic velocity is expected to be 10 times higher. This effect results in more homogeneous deposits and the thickness will depend on the deposit time.

In this paper, the use of different stabilizing agents such as surfactants and biopolyelectrolytes with different ionic nature and chain length was proposed to improve the stability of the TiO₂ dispersions.

On the other hand, the zeta potential was used as a strategy to predict the performance of the EPD process. The profiles of $\zeta = f(\text{pH})$ and $\zeta = f(\text{dose stabilizing agent})$ were made as a strategic guide to establish the best conditions of the EPD, in order to achieve homogeneous deposits in an efficient way (short times, mass yield, sufficient adhesion, and resistant to corrosion). These TiO₂ coatings have potential uses in biomedical applications, water treatment, and photocatalytic materials.

2. Experimental

2.1. Metallographic preparation of titanium substrates

Titanium sheets were used as a substrate for their high mechanical resistance and corrosion, sectioned in square pieces with dimensions 1 × 1 cm and 0.1 cm thick for the cathode and 3 × 3 cm and 0.1 cm for the anode.

2.2. Profiles of $\zeta = f(\text{pH})$ of TiO₂ and different stabilizing agents

The surface charge density, isoelectric point, and stabilizing agents-dosing strategy for the formulation of TiO₂ dispersion were determined with the profiles $\zeta = f(\text{pH})$. The zeta potential measurement was performed using the SZ-100 of Horiba Scientific equipment based on studies by López-Maldonado et al. [23, 24].

2.3. Colloidal titration of TiO₂ dispersions

The profiles of $\zeta = f(\text{stabilizing agent dose})$ were performed to determine the dose of the stabilizing agent and improve the stability of the TiO₂ dispersion. The TiO₂ dispersions were prepared with water and water/ethanol mixtures (90:10 and 50:50) using surfactants of different chemical nature such as CTAB, SDS, Betaine, and Triton X-100 and a cationic

biopolyelectrolyte chitosan (Ch), see **Figure 1**. The nominal concentration of TiO_2 was kept fixed at a value of 0.1% wt, while the concentration of the dispersing agents was varied.

The zeta potential measurements were approximated with the equipment called Stabino Particle Charge Mapping.

The stabilizing agents used in the colloidal titration of the TiO_2 dispersion are shown in **Table 1**.

2.4. EPD process of TiO_2 with stabilizing agents

To assign the function of each electrode in the EPD cell (anode or cathode), it was necessary to measure the zeta potential of the dispersed particles of each formulation, before the experiment (see **Figure 2**). All experiments were performed in a conventional 2-electrode electrophoresis cell, with a capacity of 50 mL. All TiO_2 dispersions were prepared from 40 mL of a TiO_2 0.1 wt. % (water) dispersion and then 4 mL of each stabilizing agent 1 wt. % was added, achieving a weight ratio of stabilizing agent to TiO_2 of 1:1. For the EPD process, a potential difference of 10 V and an electrodeposition time of 1 h were used. Working electrodes and

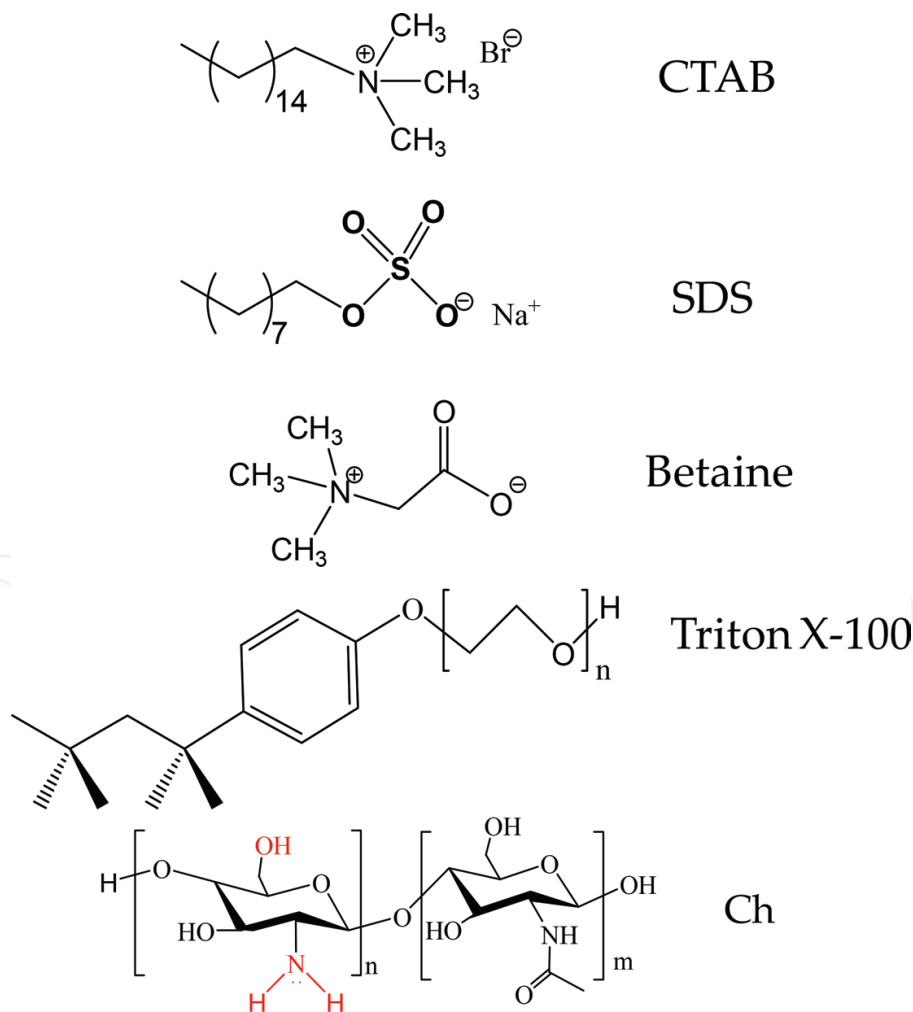


Figure 1. Chemical structure of stabilizing agents.

Dispersion	Stabilizing agent	Type of stabilizer
TiO ₂	SDS	Anionic
	CTAB	Cationic
	Triton X-100	No ionic
	Betaine	Amphoteric
	Ch	Biopolyelectrolyte

Table 1. Stabilizing agents used in the colloidal titration of the TiO₂ dispersion.

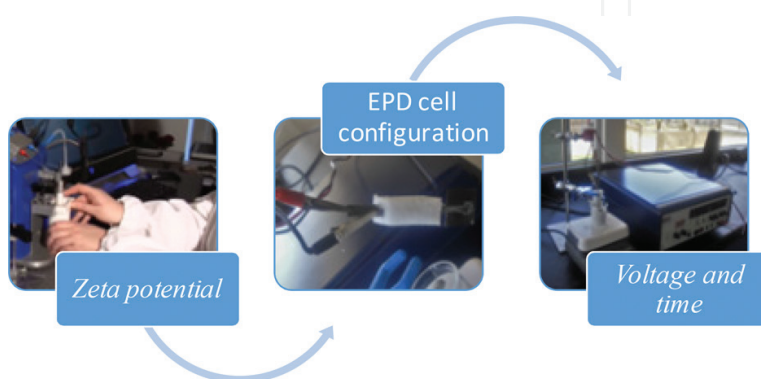


Figure 2. Experimental strategy for making TiO₂ coatings by EPD.

titanium counter electrodes were used with an area of 1 and 9 cm², respectively. All TiO₂ electrodeposits were carried out under pressure and at room temperature.

2.5. Physicochemical characterization of TiO₂ coatings

Electrodeposits of TiO₂ obtained on Ti sheets, were characterized by Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, and scanning electron microscopy (SEM). FTIR spectra of samples were recorded using a Nicolet FT-IR spectrometer. The SEM-EDS analysis was performed on SEM (ZEISS EVO-MA15), equipped with an EDS (energy dispersive spectroscopy) BRUKER detector microscope to observe the composition.

3. Results and discussion

3.1. Profiles of $\zeta = f(\text{pH})$ of TiO₂ and different stabilizing agents

The zeta potential is a parameter by electrochemical nature that allows to study and predict the interactions occurring at the molecular level between the colloidal particles TiO₂ and the different stabilizing agents, also it indicates the degree of stability of dispersion in an aqueous medium from the point electrically. The aim is to employ ζ measurements to know and understand the behavior of the type of stabilizing agents in the EPD process performance.

In **Figure 3**, the behavior of the surface charge density of TiO_2 particles and stabilizing agents is shown. TiO_2 has an anionic character, according to the zeta potential = -7.8 mV, which remains constant at pH 4–11. This implies that by electrostatic interactions, the TiO_2 can interact with the stabilizing agents of opposite charge. Chitosan presents its isoelectric point ($\zeta = 0$) at pH = 6.5, at pH lower than the IEP, shows a cationic character and at pH > IEP, the chitosan becomes an insoluble material and precipitates.

The CTAB presents a cationic character at a pH of 3–11 ($\zeta = 12.0$ mV), this is attributed to the functional group of the surfactant that maintains its positive charge in this pH range. Similarly, the SDS presents a constant charge density, $\zeta = -12.0$ mV at pH 3–11, but of anionic character due to the functional group, it has in its structure. As expected, the Triton X-100 showed a nonionic character ($\zeta = -3.0$ mV), according to the zeta potential value very close to zero, throughout the pH range.

Betaine, being an amphiphilic compound, presented an isoelectric point at pH = 3.0 and another at pH = 12.0, corresponding to the two types of functional groups it has in its structure.

It is well known that an excess or lack of ions on the surface of a material such as TiO_2 causes low mobility and therefore, deficiency of fixation on the surface of the metal electrode to be coated. For this reason, a better understanding of the surface properties of a dispersion, such as the profiles $\zeta = f(\text{pH})$, may lead to improved surface performance of the material.

3.2. Colloidal titration of TiO_2 dispersions

Considering the profiles of $\zeta = f(\text{pH})$ of the stabilizing agents and of TiO_2 , various formulations can be developed in which the TiO_2 can have a greater stability and a positive or

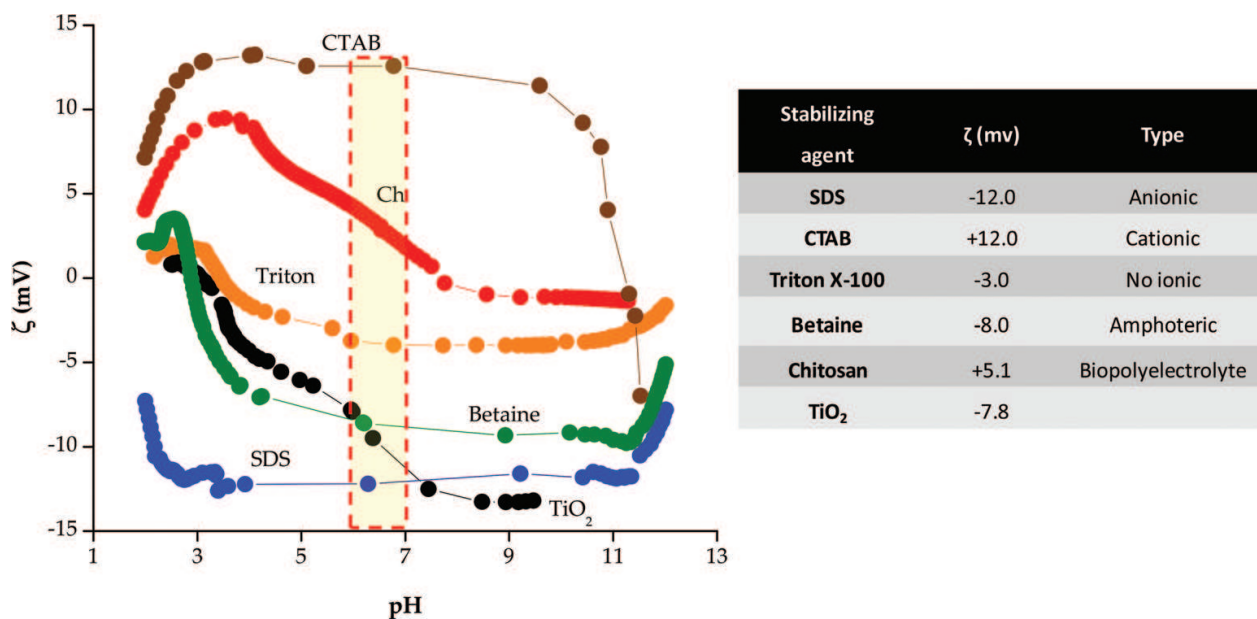


Figure 3. Profiles of $\zeta = f(\text{pH})$ of TiO_2 and different stabilizing agents.

negative surface charge density. Additionally, this implies that we can perform an anodic or cathodic electrodeposit, depending on the application.

The addition of a stabilizing agent seeks that the zeta potential value of TiO₂ ($\zeta = -7.8$ mV) moves farther from $\zeta = 0$ mV, that is, becomes more negative or very positive. This allows the TiO₂ particles to be more stable and avoid the sedimentation phenomenon.

In this work, only the characteristics of the TiO₂ electrodeposits with chitosan are discussed, however, as mentioned above, there are a series of options to perform the coatings using different stabilizing agents and evaluate their physicochemical properties based on their application.

In **Figure 4**, the profiles of $\zeta = f$ (stabilizing agent dose) of the dispersion of TiO₂ 0.1 wt. % are shown.

The addition of SDS and betaine did not significantly increase the stability of TiO₂ particles, which could be expected since they are negatively charged density compounds and would increase the repulsion forces of TiO₂ particles. The addition of Triton X-100 caused a decrease of $\zeta = -7.8$ mV TiO₂ at $\zeta = -3.0$ mV, at a dose of 11 mg Triton X-100.

On the other hand, the addition of the cationic stabilizing agents, CTAB and Ch, caused an inversion of the surface charge density of the TiO₂ particles with a dose of 4 mg. With the CTAB, a $\zeta = 9.0$ mV was reached, while with Ch, a $\zeta = 6.0$ mV, this difference is attributed to the CTAB having a higher surface charge density.

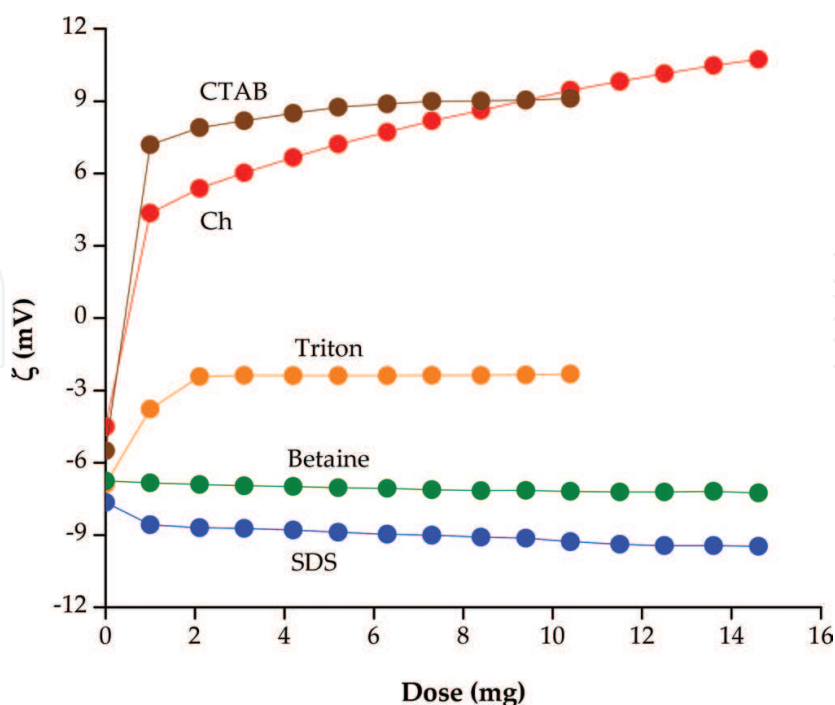


Figure 4. Profiles of $\zeta = f$ (stabilizing agent dose) of the dispersion of TiO₂ 0.1 wt. %.

For the present research, it is desired zeta potential values that guarantee stability to achieve a more homogeneous deposit (in terms of grain size and roughness). This indicates that controlling the doses of dispersing agent in such a way as to obtain values of zeta potential farthest from zero will cause the attraction force between the particles to decrease and, in turn, increase the force of attraction toward one of the poles of the electrophoretic cell. This effect is also reflected in a lower voltage demand in the electrophoretic cell and therefore the elimination of electrolysis reactions at the electrodes.

3.3. EPD process

In **Figure 5**, the effect of the electrodeposition time on the deposited TiO_2 -Ch mass is shown. It is observed that 6 mg are deposited in the first 30 min, in a longer time the amount of deposit shows an exponential behavior (**Figure 6**).

3.4. Evaluation of the Ti/TiO_2 -CTAB and Ti/TiO_2 -chitosan coating

The SEM images and the corresponding chemical microanalysis of the Ti/TiO_2 coating prepared by electrophoresis are presented in **Figure 7**. In the images of **Figure 7a**, the ceramic type structure of TiO_2 -CTAB is observed, morphologically very different from the plastic type structure obtained by impregnation of the chitosan in the layer shown in **Figure 7b**.

EDX elemental analysis indicates the presence of titanium and oxygen (TiO_2) on the surface of the electrodes. In addition, carbon signals suggest the presence of CTAB and chitosan from the dispersions. **Figure 8** shows the EDX spectra corresponding to Ti/TiO_2 -CTAB and Ti/TiO_2 -chitosan electrodes obtained by 10 V electrodeposits.

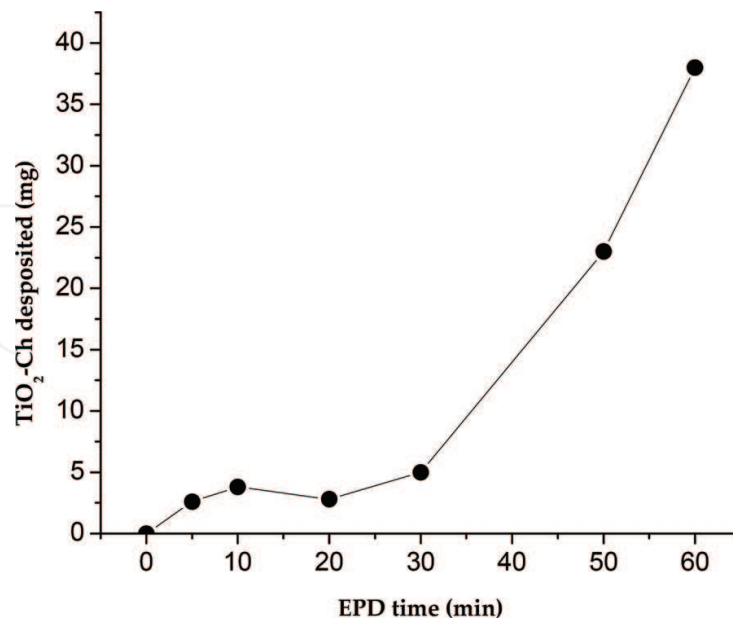


Figure 5. Influence of the electrodeposition time on the coating mass of TiO_2 .

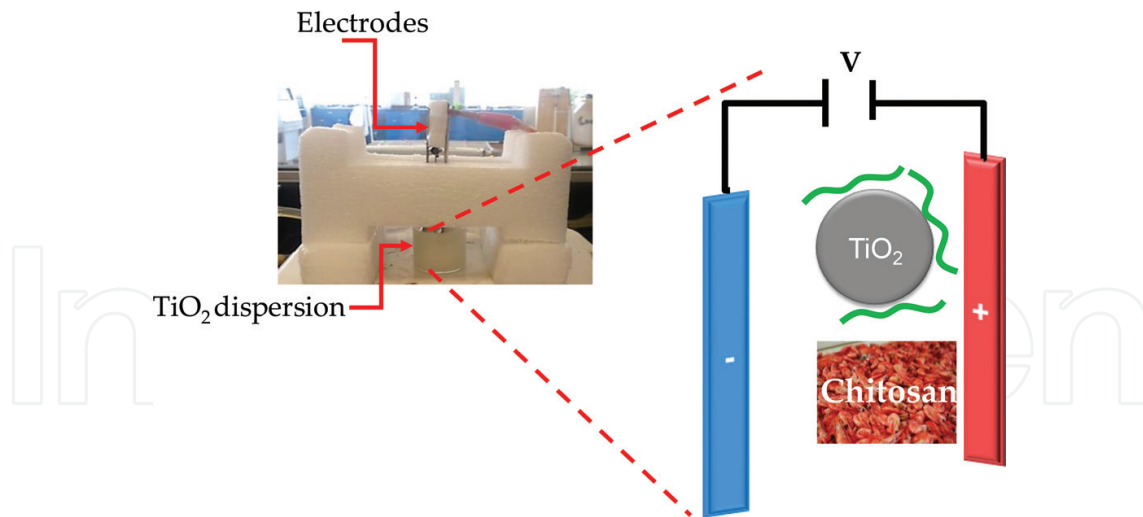


Figure 6. Schematic representation of the interface model for the EPO process of TiO_2 using chitosan.

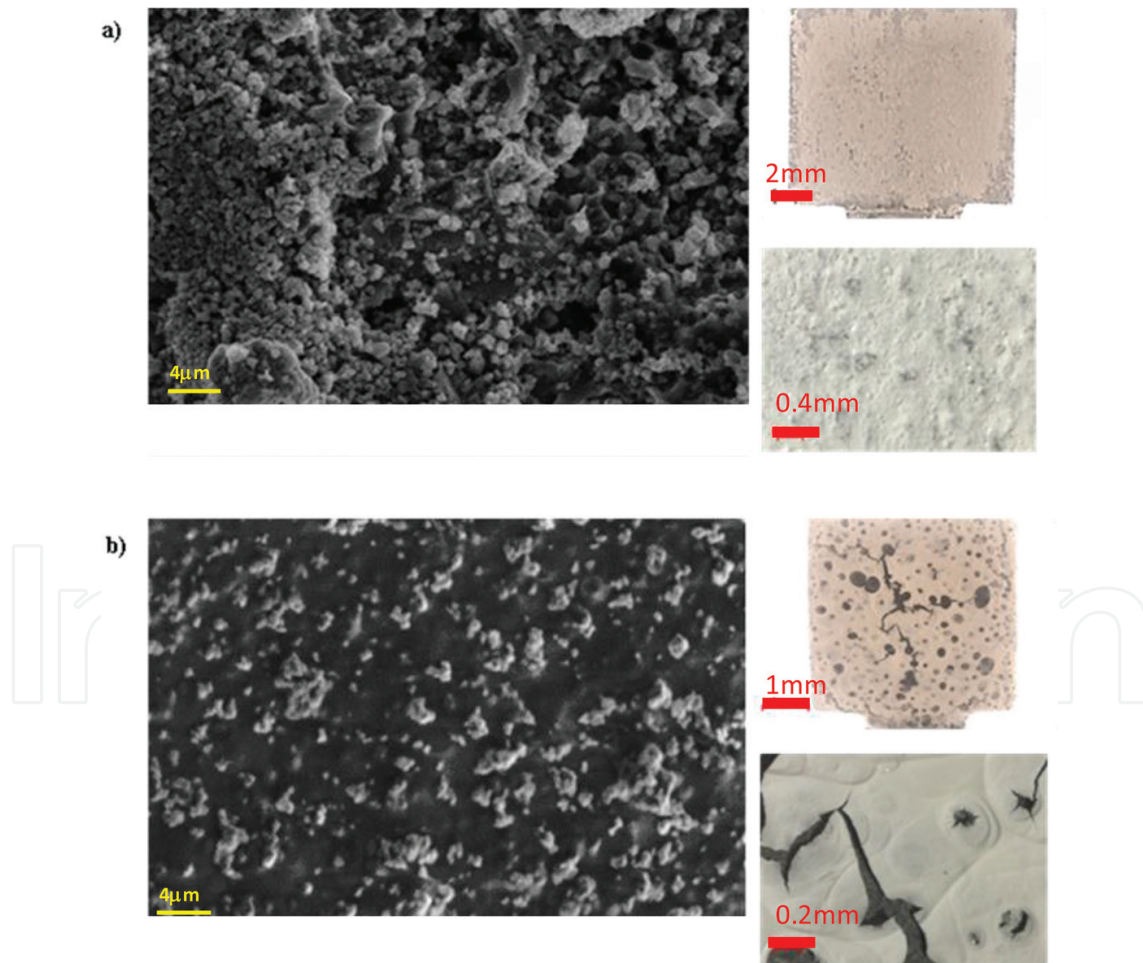


Figure 7. Micrographs of the EPD deposits with the dispersions of (a) TiO_2 -CTAB and (b) TiO_2 -chitosan.

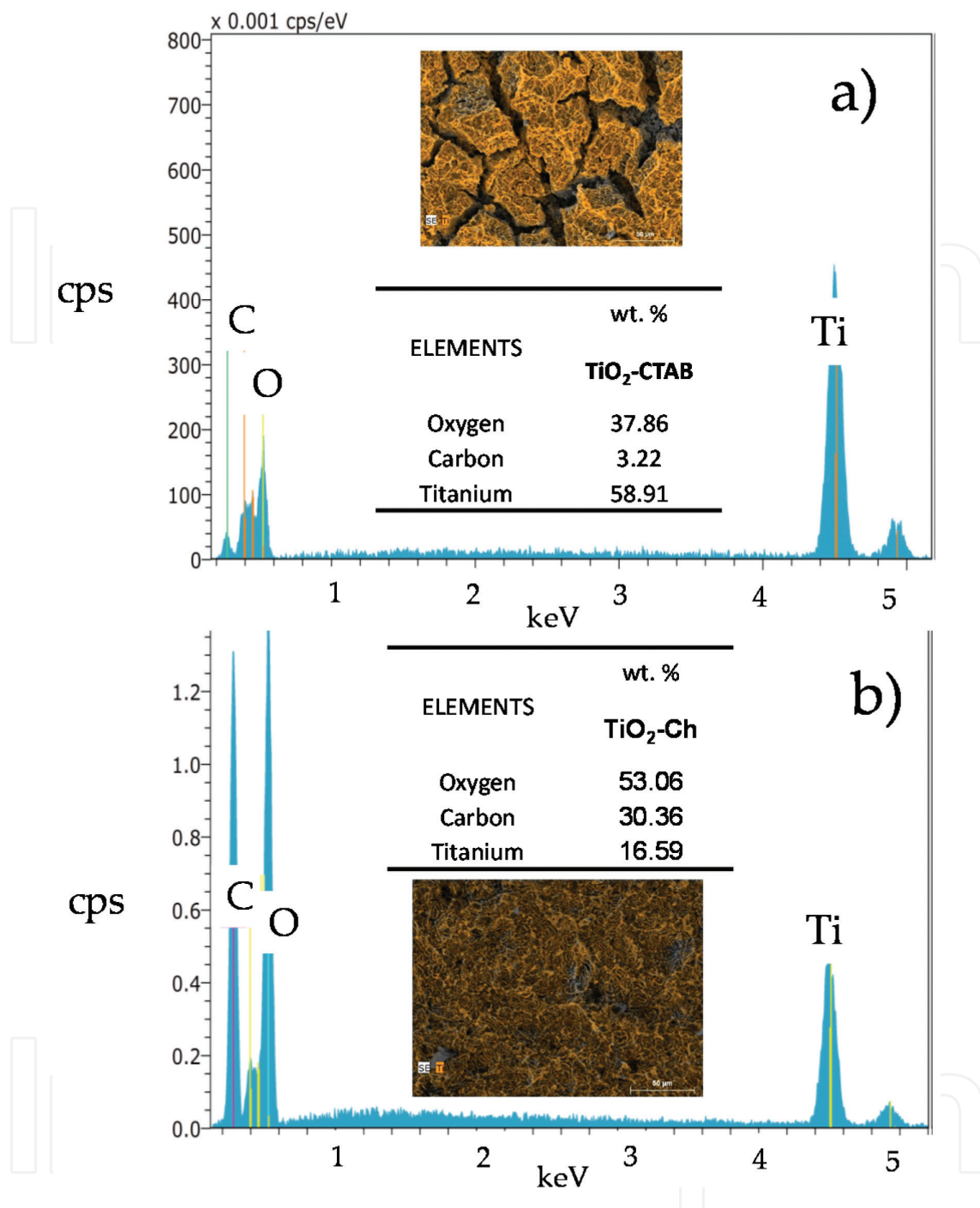


Figure 8. Spectrum of surface chemical analysis by EDX of the coatings with the dispersions of (a) TiO₂-CTAB and (b) TiO₂-Chitosan.

The analysis of the chemical composition of the electrodes showing a higher percentage by weight of carbon by the coating TiO₂-chitosan, this is attributed to the molecular weight of the chitosan that is above the CTAB.

In **Figure 9**, the FTIR spectra of the TiO₂-Ch/Ti coating are shown using EPD (time = 5 min, 10 V) and the chitosan, the coating spectrum shows a wide absorption between 3350 and 3270 cm⁻¹ to a combination of ways to stretch the OH and NH bonds in the chitosan and

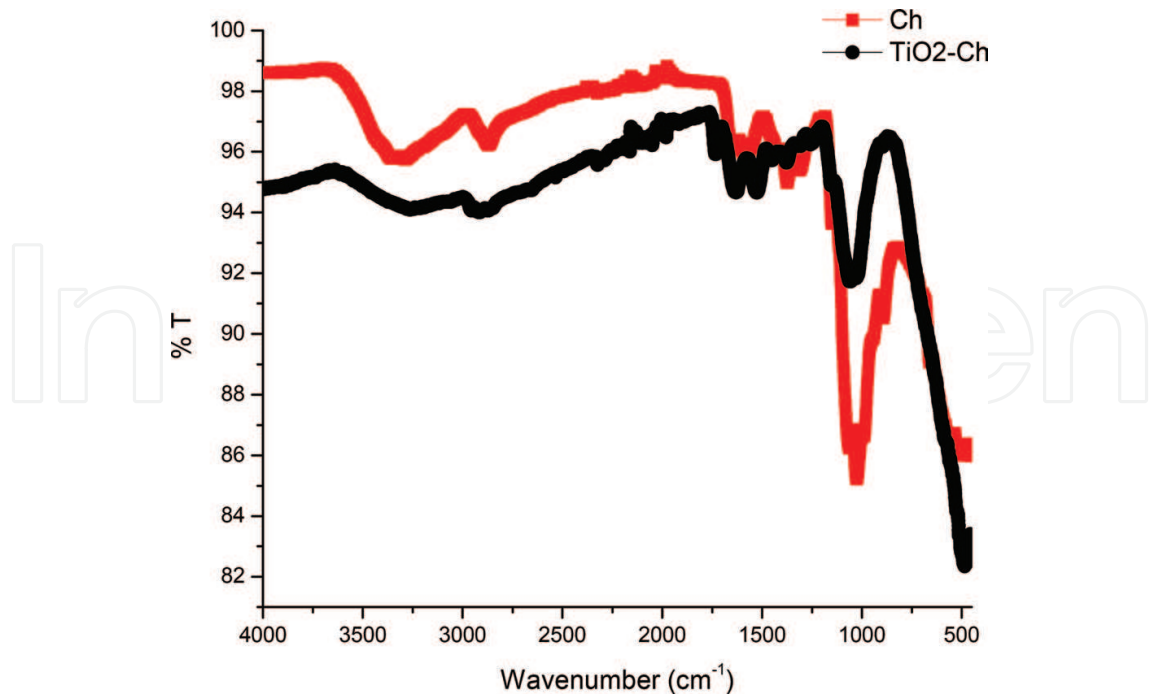


Figure 9. Micrographies of the EPD deposits with the dispersions of (a) TiO₂-CTAB and (b) TiO₂-chitosan.

hydrogen bonds between the polysaccharide chains. The band at 1650 cm⁻¹ is assigned to the amine group of stretching vibration C=O (amine I) located in the acetylated chitosan units. The band at 1600 cm⁻¹ is the result of the signal corresponding to amine II and the bending vibration NH (amine II). These signals confirm the presence of the chitosan chains with the TiO₂ particles in the Ti substrate.

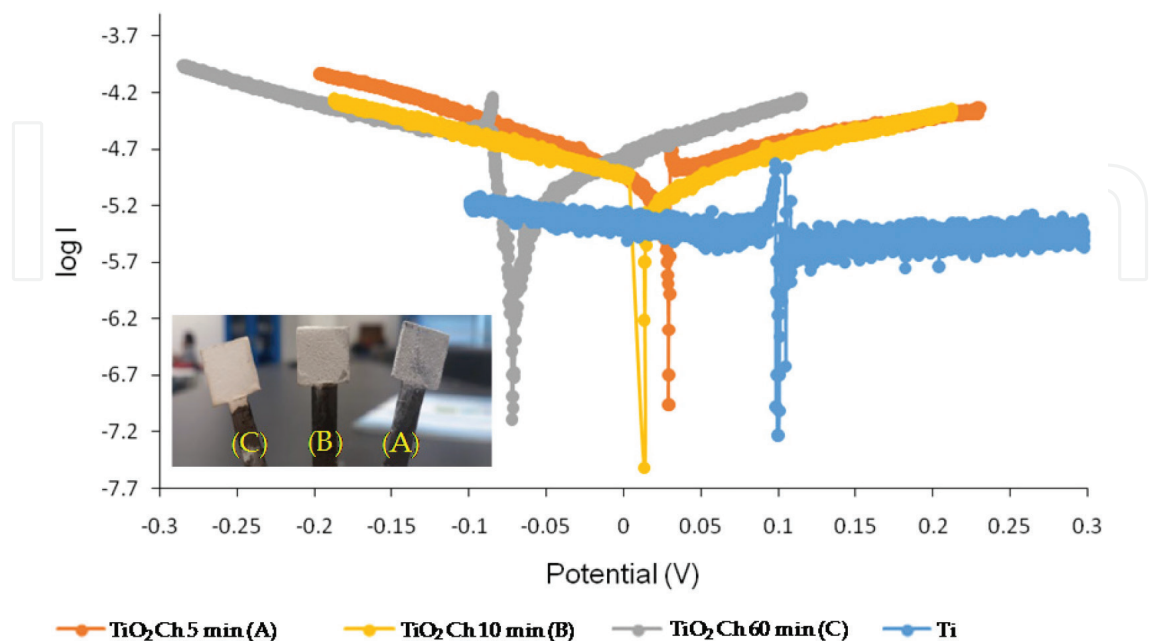


Figure 10. Polarization curves of the TiO₂-Ch electrodes in 0.5 M sulfuric acid.

In **Figure 10**, it can be seen that all TiO₂-chitosan coatings show a lower voltage compared to the Ti electrode, which means that TiO₂-chitosan composite coatings tend to oxidize more easily, because the more negative the difference of the slower the oxidation reaction of the species to the coating, and the faster the reduction reaction of the species to the coating, therefore, higher protective properties are obtained than the Ti electrode (**Figure 6**).

However, the growth of the TiO₂-chitosan layer appears to displace the overpotentials more negatively. The fact that the chitosan layer does not reduce the corrosion potential may be due to its reaction with the medium, due to the degradation effects of chitosan.

4. Conclusions

The use of the zeta potential measurements allows to determine the pH range in which a stabilizing agent is effective and can interact with the TiO₂ particles to improve its stability. Through the profiles of $\zeta = f$ (stabilizing agent dose), the exact amount that is required to achieve a surface charge density that improves the performance of the electrodeposition process is determined. Additionally, the zeta potential is a guide parameter that allows addressing if the electrophoretic deposition process is cathodic or anodic, using either a surfactant or a biopolyelectrolyte.

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Conflict of interest

The authors state that there is no conflict of interest.

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