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Co, Cu, Fe, and Ni Deposited over TiO$_2$ and Their Photocatalytic Activity in the Degradation of 2,4-Dichlorophenol and 2,4-Dichlorophenoxyacetic Acid

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Abstract: Pure TiO$_2$ synthesized by the sol-gel method and subsequently deposited at 5% by weight with Co, Cu, Fe, and Ni ions by the deposition–precipitation method was studied as photocatalysts. The nanomaterials were analyzed by SEM, TEM, UV-Vis DRS, DRX, Physisorption N$_2$, and XPS. The SEM and TEM images present a semi-spherical shape with small agglomerations of particles and average size between 63 and 65 nm. UV-Vis results show that a reduction below 3.2 eV exhibits a redshift displacement and increment in the optical absorption of the nanoparticles promoting the absorption in the UV-visible region. XRD spectra and analysis SAED suggest the characteristic anatase phase in TiO$_2$ and deposited materials according to JCPDS 21-1272. The specific surface area was calculated and the nanomaterial Ni/TiO$_2$ (21.3 m$^2$ g$^{-1}$) presents a slight increment when comparing to TiO$_2$ (20.37 m$^2$ g$^{-1}$). The information generated by the XPS spectra present the deposition of metallic ions on the support and the presence of different valence states for each photocatalyst. The photocatalytic activity was carried out in an aqueous solution with 80 mg L$^{-1}$ of 2,4-D or 2,4-DCP under UV light (285 nm) with 100 mg L$^{-1}$ of each photocatalyst for 360 min. The nanomaterial that presented the best efficiency was Ni/TiO$_2$, obtaining a degradation of 85.6% and 90.3% for 2,4-D and 2,4-DCP, respectively. Similarly, this material was the one that presented the highest mineralization, 68.3% and 86.5% for 2,4-D and 2,4-DCP, respectively. Photocatalytic reactions correspond to the pseudo-first-order Langmuir–Hinshelwood model.

Keywords: titanium dioxide; photocatalysis; deposition-precipitation; organic herbicides; photocatalytic activity

1. Introduction

Chlorophenols are a group of pollutants commonly found in wastewater and represent a health concern due to their toxicity, chemical stability, and low biodegradability [1]. 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4-dichlorophenol (2,4-DCP) have been reported as priority pollutants by the Environmental Protection Agency (EPA) and World Health Organization (WHO) for the damage caused to human health and the environment [2,3]. These compounds are widely used in the development of personal care, textile, petrochemical, and agricultural products [4,5]. Mountassif et al. observed a bioaccumulation of 2,4-D (91.7%) in the water since not being absorbed into the soil; this is in accordance
with high level reports of organic compounds from various countries [6]. In Mexico, these have been used mainly as material for the production of insecticides, pesticides, and herbicides [7,8]. For its part, a study carried out in 2006 in Chapala and Sayula Lakes by Reynoso Silva et al. report on the 2006 drought, a concentration 10 times higher (0.02 ppm) in Chapala compared to Sayula (0.002 ppm) in the liver of Goodea atripinnis, a species of fish endemic to the area. In that same year, in the rainy season, a concentration of 0.05 ppm is identified in Chapala and 0.05 ppm in Sayula due to the agricultural activity [9]. The use of conventional methods for the removal of pollutants in water have been investigated, and their residuals are removed with complementary treatments [10,11].

In the last decade, the Advanced Oxidation Processes (AOPs) technologies and heterogeneous photocatalysis have emerged as an efficient alternative for wastewater treatment through the use of photocatalysts such as CdS, ZnO, ZnS, Fe$_2$O$_3$, WO$_3$, and TiO$_2$ [12–14]. TiO$_2$ is a good photocatalyst due to its chemical stability, nontoxicity, low-cost, abundance, and acceptable efficiency for the degradation of pollutants in water. However, its wide band gap (~3.2 for anatase phase) limits its response to the UV-light range, promoting high electron–hole pair recombination and poor photocatalytic activity [15,16]. In this context, the improvement of its structural, morphological, optical, and surface properties is essential to increase the efficiency of the photocatalytic processes, which could be carried out by doping with other inorganic compounds and synthesizing different chemical routes [17–20].

Currently, several approaches have been studied to enhance the photocatalytic activity of TiO$_2$ for wastewater treatment, including metal doping using Al, Cr, Ag, Au, Pt, Mn, Cu, Fe, Co, and Ni, attributed with the structural and physicochemical parameters modification of TiO$_2$ [5,17,21,22]. Previous studies suggested that the incorporation of copper ions into TiO$_2$ matrix provides an increase in the photocatalytic activity for the degradation of organic pollutants (stearic acid), associated with the modification of the UV-light absorption wave, reducing energy band gap (Eg) values [23]. Furthermore, it was found that the doping of iron into TiO$_2$ allows a decrease in the crystallite size, modifies the absorption wavelength, and shortens the band gap energy [24]. Anju et al. reported similar trends in the degradation of 2,4-DCP using pure TiO$_2$ as a support and doping with cobalt and nickel ions [25].

Therefore, this work aimed to evaluate the effect of metal ions Co$^{2+}$, Cu$^{2+}$, Fe$^{3+}$, and Ni$^{2+}$ (5% wt.) using the TiO$_2$ photocatalyst as support by the deposition–precipitation method. The synthesized samples were characterized with various techniques such as SEM, TEM, UV-Vis DRS, DRX, FTIR, Physiosorption N$_2$, and XPS. The deposited-TiO$_2$ nanomaterials were evaluated through the heterogeneous photocatalysis to measure the photocatalytic activity in the degradation and mineralization of 2,4-D and 2,4-DCP.

2. Experimental

2.1. Chemical Reagents

Titanium (IV) butoxide reagent grade C$_{16}$H$_{36}$O$_4$Ti, 97% purity; Urea, CH$_4$N$_2$O reagent grade 99% purity; 2,4-Dichlorophenol, reagent grade C$_6$H$_4$Cl$_2$O, 99% purity; polyethylene glycol (PEG), 98% purity and 2,4-Dichlorophenoxyacetic acid, reagent grade Cl$_2$C$_6$H$_3$OCH$_2$CO$_2$H, 97% purity; these reagents were obtained from Sigma-Aldrich. Cobalt (II) nitrate hexahydrate, Co(NO$_3$)$_2$ * 6H$_2$O reagent grade 92% purity; Cupric (II) Nitrate Hydrated, Cu(NO$_3$)$_2$ * 3H$_2$O reagent grade 92% purity; Iron (III) Nitrate nonahydrate Fe(NO$_3$)$_3$ * 9H$_2$O reagent grade 92% purity; Nickel (II) nitrate hexahydrate, Ni(NO$_3$)$_2$ * 6H$_2$O reagent grade 92% purity; these reagents were obtained from Meyer (Blue Springs, MO, USA). Ammonium hydroxide NH$_4$OH reagent grade 28–30% purity was obtained from Jalmek (San Nicolás de los Garza, Mexico), and deionized water was obtained from the Golden Bell Company (Bell, CA, USA).

2.2. Synthesis of TiO$_2$ Nanoparticles

The sol-gel method was used with some modifications to obtain TiO$_2$ nanoparticles from the precursor C$_{16}$H$_{36}$O$_4$Ti [26]. In a three-necked flask, 140 mL of ethanol with 14 g of Titanium (IV) butoxide and 2 g of PEG were kept under magnetic stirring at 300 rpm. The
solution was brought to a neutral pH by adding NH\textsubscript{4}OH (1 M) drop by drop. The mixed was then refluxed at 80 °C for 2 h; it was sonicated for 1 h and cooled to 0 °C for 12 h. The gel obtained was dried at 100 °C and calcined at 500 °C for 5 h in a static air atmosphere (heating rate of 2 °C/min).

2.3. Deposited-TiO\textsubscript{2} Nanoparticles

The preparation of the deposited-TiO\textsubscript{2} materials with different ions (5% wt.) was carried out by the deposition–precipitation method with urea [17]. The TiO\textsubscript{2} support was dried for 12 h at 100 °C before deposition of the Co ions. The metal ions (0.0042 M) used as a Co-precursor, and urea (0.42 M), were mixed in 100 mL of distilled water at room temperature under magnetic stirring until homogenization. Subsequently, 2 g of the TiO\textsubscript{2} support were added to the mixture. The suspension was kept in a vigorous stirring at 80 °C in the absence of light for 24 h. The solution was washed and centrifuged four times to remove excess ions deposited over support material. Once the solid was obtained, it was dried at 100 °C for 2 h at room temperature. This procedure was repeated to obtain the Cu, Fe, and Ni deposited-TiO\textsubscript{2} materials.

2.4. Materials Characterization

The micrographs of the materials were examined by scanning electron microscopy (Tescan, MIRA 3LMU, United Kingdom) operated at 20 kV. The microstructure of deposited-TiO\textsubscript{2} was studied by means of high-resolution transmission electron microscopy (Jeol, Peabody, MA, USA) operated at 200 kV. The absorbance of modified-TiO\textsubscript{2} nanomaterials was measured using a UV-Vis DRS spectrophotometer (Shimadzu UV-2600, Tokyo, Japan) in the wavelength range of 200 and 900 nm. The band gap energy (plot) was calculated using the Tauc plot method [27]:

\[
\frac{(\alpha \cdot h\nu)^1}{\gamma} = B(h\nu - E_g) \tag{1}
\]

where \(h\) is the Planck constant, \(v\) is the photon’s frequency, \(E_g\) is the band gap energy, and \(B\) is a constant, based on the assumption that the absorption coefficient \(\alpha\) can be expressed. The Kubelka–Munk function is used to determine the measure of band gap energy through the diffuse reflectance spectra.

The information on phase, crystallite size, and lattice parameters values of the nanomaterials were determined by X-ray diffraction (Panalytical diffractometer, Empyrean, Almelo, the Netherlands) equipped with Cu K\textalpha radiation (\(\lambda = 0.154\) nm). The diffraction patterns were obtained from 10\textdegree to 90\textdegree (2\theta) with a scan rate of 0.02\textdegree/0.2 s. The average crystal size was determined using the Scherrer equation:

\[
D = \frac{k\lambda}{\beta \cos \theta} \tag{2}
\]

where \(D\) is the crystal size, \(k\) is the form factor (0.89), \(\lambda\) is the wavelength of Cu K\textalpha radiation (0.154 nm), \(\beta\) is the width evaluated at mid-high of the most intense diffraction peak, and \(\theta\) is the Bragg angle.

The inter-planar distance (\(d\)) was evaluated with Bragg’s law:

\[
d (\text{Å}) = \frac{n\lambda}{2 \sin \theta} \tag{3}
\]

The FTIR spectra were recorded on an FTIR (Thermo Fisher Scientific, Nicolet iS5, Tokyo, Japan) Spectrometer (4000–200 cm\textsuperscript{-1}) using attenuated total reflectance (ATR) with a diamond waveguide (XR model). A detector of fast recovery, deuterated triglycine sulfate (DTGS) (standard) was used for the analysis. The FTIR spectra were recorded at room temperature, with 24 scans and 4 cm\textsuperscript{-1} of resolution. The specific surface area was obtained by the Brunauer–Emmett–Teller method (BET), and the pore size distribution was obtained following the Barrett–Joyner–Halenda (BJH) method.
Micromeritics analyzer (TriStar II Plus, USA) was used for measurement of the deposited-
TiO\(_2\) the surface area, pore volume, and pore size by nitrogen adsorption–desorption. The samples were degassed at 200 °C for 2 h, under vacuum. Nitrogen adsorption isotherms were measured at liquid nitrogen temperature (77 K), and nitrogen pressures ranging from \(10^{-6}\) to 1.0 \(P/P_0\). The XPS spectra were collected using a SPECS PHOIBOS 150 spectrometer by using Al K\(\alpha\) monochromatic (1486.6 eV) radiation as the excitation source. The XPS analysis was carried out at ambient temperature and pressures typically in the order of less than \(10^{-6}\) Pa. The binding energy shifts due to surface charging were corrected using the binding energy of carbon (C 1s 284.8 eV) \[28\].

2.5. Photocatalytic Activity

The photocatalytic properties of deposited-TiO\(_2\) nanomaterials (Co/TiO\(_2\), Cu/TiO\(_2\), Fe/TiO\(_2\) and Ni/TiO\(_2\)) were studied through the degradation of 2,4-D and 2,4-DCP in a typical kinetic reaction experiment. A glass batch reactor provided with a cooling medium, and a UV-lamp of 1 mW cm\(^{-2}\) placed inside a quartz tube was used. The reactor was loaded with 330 mL of deionized polluted water with 80 mg L\(^{-1}\) of 2,4-D or 80 mg L\(^{-1}\) 2,4-DCP, and 100 mg L\(^{-1}\) of deposited-TiO\(_2\) as a catalyst. The degradation curves were obtained by measuring the evolution of absorbance maximum (at 283 and 285 nm for 2,4-D and 2,4-DCP, respectively) as a function of time (every 30 min up to 360 min) using a UV-Vis (Shimadzu UV-2600, Tokyo, Japan) spectrophotometer with scans from 200 to 900 nm.

The total organic carbon in the samples was measured using a TOC-LCSN equipment (Shimadzu, model), and calculated applying Equation (2):

\[
\text{TOC} = \text{TC} - \text{IC}
\]

where TOC is the amount of total organic carbon (mg L\(^{-1}\)), TC is the amount of total carbon (mg L\(^{-1}\)), and IC inorganic carbon (mg L\(^{-1}\)) in aqueous solution.

3. Results

3.1. Scanning Electron Microscopy (SEM) Analysis

Figure 1 shows the surface morphology of pure TiO\(_2\) and deposited-TiO\(_2\) photocatalyst. The TiO\(_2\) nanoparticles (Figure 1a) exhibited semi-spherical form with some aggregates with a homogeneous distribution and sizes <100 nm. The Co/TiO\(_2\) (Figure 1b) exhibited uniform small semi-spherical nanoparticles similar to those reported in literature \[29\], while the Cu/TiO\(_2\) (Figure 1c) presented a semi-spherical shape and homogeneous distribution, in agreement with those reported by Qureshi et al. \[30\]. The addition of the iron ion (Figure 1d) to TiO\(_2\) does not show significant morphological changes, and the semi-spherical shape is still maintained with small agglomerations of particles \[31\]. Figure 1d shows the result of the doping of TiO\(_2\) with Ni ions, where small agglomerations of particles with a semi-spherical shape can be observed with a uniform size distribution; these results can be compared with those presented by Kunnamareddy et al. \[32\]. In general, the incorporation of the different doping ions such as Co, Cu, Fe, and Ni does not significantly affect the typical morphological features of TiO\(_2\), mainly associated with the deposition–precipitation method used during the synthesis process \[14,17\].
3.2. Transmission Electron Microscopy (TEM) Studies

The images show that the materials exhibited a semi-spherical form with some superficial agglomerations and sizes less than 100 nm of diameter (Figure 2). The average size by nanoparticle is 64.18 ± 18.74 nm (TiO$_2$), 63.27 ± 16.55 nm (Co/TiO$_2$), 65.67 ± 13.28 nm (Cu/TiO$_2$), 68.03 ± 13.28 nm (Fe/TiO$_2$), and 68.50 ± 20.75 nm (Ni/TiO$_2$). The distribution histograms of particle sizes for all samples are presented in (Figure 2). The diameter of the particles was estimated by measuring 100 nanoparticles on the TEM images using ImageJ software (Java 1.8.0_172 64 bits, Wayne Rasband, University of Wisconsin, USA). The average particle diameter is 18.53 ± 6.72 nm (TiO$_2$), 20.27 ± 6.02 nm (Co/TiO$_2$), 15.36 ± 3.57 nm (Cu/TiO$_2$), 16.44 ± 3.71 nm (Fe/TiO$_2$) and 24.66 ± 6.73 nm (Ni/TiO$_2$). Nguyen et al. found that the crystallite diameter for Pd-doped TiO$_2$ is in the range of 12–28 nm by measuring 20 particles using the ImageJ program [15]. It has been reported that nanoparticles with size ≤ 100 nm are more active against organic pesticides than higher nanoparticles, associated with an increase in surface area [33,34].

The selected area electron diffraction (SAED) pattern corresponded to TiO$_2$ and modified TiO$_2$ (Figure 3). The images revealed the crystalline structure that corresponds to the anatase phase of support (TiO$_2$) according to JCPDF 21-1272 [1]. The rings show good homogeneity in shape; however, some rings of the samples show discontinuity due to the formation of larger crystallites, as demonstrated by Maurya and Bhatia et al. [35]. The TEM analytical results indicate a good dispersion of the ion metallic (Cu$^+$, Ni$^+$) over the surface of TiO$_2$ through the deposition–precipitation process corroborating the results of the SEM analysis.
Figure 2. Cont.
Figure 2. Transmission Electron Microscopy images and particle diameter of photocatalysts: (a) TiO$_2$; (b) Co/TiO$_2$; (c) Cu/TiO$_2$; (d) Fe/TiO$_2$; and (e) Ni/TiO$_2$.

Figure 3. SAED pattern images of: (a) TiO$_2$; (b) Co/TiO$_2$; (c) Cu/TiO$_2$; (d) Fe/TiO$_2$; and (e) Ni/TiO$_2$.

Figure 4 shows the UV-Vis diffuse reflectance spectra of the TiO$_2$ and deposited-TiO$_2$ photocatalysts. TiO$_2$ exhibited a strong absorption band between 400 and 450 nm (Figure 4a), which is characteristic of O$_2$p $\rightarrow$ Ti$_3$d transitions in the tetrahedral structure or TiO$_2$ in its anatase phase [36]. The TiO$_2$ NPs present two shoulders around 200–250 and 250–300 nm (bands associated with bulk crystals), which may change with the incorporation of doping ions, promoting a displacement in the UV-light absorption spectra [37]. Pure TiO$_2$ exhibits an absorption band edge at 421 nm (ultraviolet absorption) [38], and similar trends were observed in Co/TiO$_2$ (416 nm), Cu/TiO$_2$ (451 nm), Fe/TiO$_2$ (443 nm), and Ni/TiO$_2$ (408 nm) samples. The band-gap (E$_g$) energies of the nanomaterials were calculated by applying the Tauc's plot method and Kubelka–Munk function [27]; results are shown in Table 1. The nanoparticles of Co/TiO$_2$ (2.80 eV), Ni/TiO$_2$ (2.85 eV), and TiO$_2$ (2.77 eV) showed similar results, unlike Cu/TiO$_2$ (2.50 eV) and Fe/TiO$_2$ (2.53 eV), which exhibited a significant reduction in E$_g$ values. It is well known that, when E$_g$ exhibits a redshift displacement, we can observe an increment in the optical absorption of the nanoparticles promoting the absorption in the UV-visible region [39,40]. In this context, a displacement of E$_g$ value in nanomaterials helps to increase their photocatalytic efficiency in the degradation of organic contaminants [41,42].
3.3. UV-VIS by Diffuse Reflectance Spectroscopy

Figure 4 shows the UV-Vis diffuse reflectance spectra of the TiO$_2$ and deposited-TiO$_2$ photocatalysts. TiO$_2$ exhibited a strong absorption band between 400 and 450 nm (Figure 4a), which is characteristic of O$_{2p}$ → Ti$_{3d}$ transitions in the tetrahedral structure or TiO$_2$ in its anatase phase [36]. The TiO$_2$ NPs present two shoulders around 200–250 and 250–300 nm (bands associated with bulk crystals), which may change with the incorporation of doping ions, promoting a displacement in the UV-light absorption spectra [37]. Pure TiO$_2$ exhibits an absorption band edge at 421 nm (ultraviolet absorption) [38], and similar trends were observed in Co/TiO$_2$ (416 nm), Cu/TiO$_2$ (451 nm), Fe/TiO$_2$ (443 nm), and Ni/TiO$_2$ (408 nm) samples. The band gap (Eg) energies of the nanomaterials were calculated by applying the Tauc’s plot method and Kubelka–Munk function [27]; results are shown in Table 1. The nanoparticles of Co/TiO$_2$ (2.80 eV), Ni/TiO$_2$ (2.85 eV), and TiO$_2$ (2.77 eV) showed similar results, unlike Cu/TiO$_2$ (2.50 eV) and Fe/TiO$_2$ (2.53 eV), which exhibited a significant reduction in Eg values. It is well known that, when Eg exhibits a redshift displacement, we can observe an increment in the optical absorption of the nanoparticles promoting the absorption in the UV-visible region [39,40]. In this context, a displacement of Eg value in nanomaterials helps to increase their photocatalytic efficiency in the degradation of organic contaminants [41,42].

Table 1. Catalyst properties

| Catalyst     | Eg (eV) | λ (nm) | Average Crystallite Size (nm) | * Standard Error | VP (cm$^{-3}$) | * | Density (g.cm$^{-3}$) | * |
|--------------|---------|--------|-------------------------------|------------------|----------------|---|----------------------|---|
| TiO$_2$      |         |        |                               |                  |                |   |                      |   |
| Co/TiO$_2$   | 2.80    | 416    | 12.35 ± 0.20                  | 0.35243          | 20.1           | 0.092 | 18.37               |   |
| Cu/TiO$_2$   | 2.50    | 451    | 10.42 ± 0.15                  | 0.35464          | 20.2           | 0.077 | 15.19               |   |
| Fe/TiO$_2$   | 2.53    | 443    | 14.23 ± 0.30                  | 0.35229          | 21.3           | 0.049 | 9.153               |   |
| Ni/TiO$_2$   | 2.85    | 408    | 13.65 ± 0.25                  | 0.35207          | 21.0           | 0.100 | 16.65               |   |

Figure 3. SAED pattern images of: (a) TiO$_2$; (b) Co/TiO$_2$; (c) Cu/TiO$_2$; (d) Fe/TiO$_2$; and (e) Ni/TiO$_2$.

Figure 4. UV-Vis spectra and determination of the band gap energies. (a) UV–vis absorption spectra of TiO$_2$ nanoparticles and photocatalyst. (b) Tauc’s plot of pure TiO$_2$ nanoparticles and photocatalyst.
3.4. X-ray Diffraction

The photocatalysts were studied by X-ray diffraction (XRD) to identify their crystalline structure and patterns of pure TiO2 and deposited-TiO2 depicted in Figure 5. The XRD pattern of TiO2 and deposited-TiO2 NPs show the characteristics peaks of the tetragonal anatase phase of TiO2 at 2θ: 25.26° (101), 37.75° (004), 48.00° (200), 53.92° (105), 55.02° (211), 62.66° (204), 68.82° (116), 70.25° (220), 75.07° (215), and 83.52° (312), according to the JCPDS 21-1272 [43,44]. In addition, the presence of the rutile phase was identified in all samples. The rutile phase for TiO2, Cu/TiO2, and Ni/TiO2 is located at 2θ degrees: 27.38°, 27.20°, and 27.39°, with the Miller index (110). Similarly, at 2θ: 44.61°, 44.60°, and 44.59°, the Miller index (215) of the rutile phase is identified for Co/TiO2, Cu/TiO2, and Fe/TiO2, according to the crystallographic card JCPDS 21-1276 [45]. The deposited-TiO2 samples do not present significant changes in the diffractogram, which can be attributed to the low content of dopant ions and their high physical dispersion in TiO2 surface [46]. Furthermore, the deposition–precipitation method with urea is widely used in metallic ions over TiO2 deposition as it provides good dispersion according to previous reports [47]. The crystallite size of TiO2–anatase was estimated by the Scherrer equation, and the results are reported in Table 1. The samples showed an average crystallite size ranging from 10 to 14 nm, suggesting that crystallite size is influenced by the element dopant dispersed in the support [48].

### Table 1. Optical and textural properties for the TiO2 and deposited-TiO2 photocatalysts.

| Catalyst | E_g (eV) | λ (nm) | Average Crystallite Size (nm) | d-Spacing (nm) | S BET (m^2 g^-1) | V_p (cm^3 g^-1) | d_p (nm) |
|----------|----------|--------|------------------------------|---------------|----------------|----------------|----------|
| TiO2     | 2.77     | 421    | 12.45 ± 0.20                 | 0.35229       | 20.37          | 0.096          | 18.83    |
| Co/TiO2  | 2.80     | 416    | 12.35 ± 0.20                 | 0.35243       | 20.1           | 0.092          | 18.37    |
| Cu/TiO2  | 2.50     | 451    | 10.42 ± 0.15                 | 0.35464       | 20.2           | 0.077          | 15.19    |
| Fe/TiO2  | 2.53     | 443    | 12.42 ± 0.21                 | 0.35284       | 18.4           | 0.051          | 11.00    |
| Ni/TiO2  | 2.85     | 408    | 14.23 ± 0.30                 | 0.35229       | 21.3           | 0.049          | 9.153    |

Notes: E_g: Band gap energy; λ: Absorbance; *: Standard error; S_BET: BET surface area; V_p: pore volume; d_p: average pore size.

![Figure 5. X-ray diffraction patterns of photocatalysts.](image-url)
Table 1 shows the value of *d*-spacing of TiO$_2$ (0.3523 nm), Co/TiO$_2$ (0.3524 nm), Cu/TiO$_2$ (0.3547 nm), Fe/TiO$_2$ (0.3528 nm), and Ni/TiO$_2$ (0.3523 nm). These values were compared with the standard values of *d*-spacing of the JCPDS 21-1276 and corroborate the anatase phase structure of TiO$_2$ and are attributed to the (101) lattice planes [45]. The variation present in the *d*-spacing between modified TiO$_2$ nanomaterials suggests the incorporation of metallic ions into the support structure [49,50]. The anatase crystalline phase present in the modified TiO$_2$ samples is an indicative of high charge mobility and low charge resistance (generation of hydroxyl radicals) of these materials, which may increase the photocatalytic activity of nanocatalysts against organic pesticides [51,52].

The unit cell parameters of pure TiO$_2$ and deposited-TiO$_2$ are listed in Table 2. The lattice parameters of the anatase tetragonal phase of TiO$_2$ (a = 3.788 Å, c = 9.524 Å) and volume (136.64 Å$^3$) consistent with the JCPDS 21-1272 card. On the other hand, deposited-TiO$_2$ samples showed are influenced in ion deposited-dependent response, the samples of Cu/TiO$_2$ (a = 3.803 Å, c = 9.561 Å, and V = 138.06 Å$^3$) and Fe/TiO$_2$ (a = 3.791 Å, c = 9.532 Å, and V = 136.99 Å$^3$) increases, while Co/TiO$_2$ (a = 3.788 Å, c = 9.520 Å, and V = 136.60 Å$^3$) and Ni/TiO$_2$ (a = 3.788 Å, c = 9.520 Å, and V = 136.60 Å$^3$) decreased compared to the TiO$_2$. This phenomenon is attributed to a well/poor dispersion of the different metallic ions on the surface of the TiO$_2$ [40]. Previous studies have shown that the photocatalytic efficiency of TiO$_2$ was improved by doping with different elements, since this process affects the particle size and the crystalline phase of the materials, achieving an adequate transfer of the photoexcited electron–hole pairs [33]. The modified TiO$_2$ samples show a slight increase in crystallite size due to metallic ions (presence of defects), which is directly related to the decrease in the band gap, that in turn, may improve their photocatalytic activity against organic pollutants [54,55].

Table 2. Unit cell parameters for the photocatalysts.

| Sample | a (Å) | c (Å) | c/a (Å) | Volume (Å$^3$) |
|--------|-------|-------|---------|----------------|
| TiO$_2$ | 3.788 | 9.524 | 2.515   | 136.643        |
| Co/TiO$_2$ | 3.788 | 9.520 | 2.513   | 136.602        |
| Cu/TiO$_2$ | 3.803 | 9.561 | 2.514   | 138.061        |
| Fe/TiO$_2$ | 3.791 | 9.532 | 2.514   | 136.991        |
| Ni/TiO$_2$ | 3.788 | 9.520 | 2.513   | 136.602        |

3.5. FT-IR Results

Figure 6 shows the FTIR spectra for the pure and deposited-TiO$_2$ nanoparticles. In Figure 6a, the FTIR spectrum of TiO$_2$ shows stretching modes around 1683 cm$^{-1}$ corresponding to the bending modes of Ti-OH water, the signals around 1557, 1507, and 1339 cm$^{-1}$ are ascribed to the vibrational modes related to the polymer alkyl chain (PEG); the first is due to the stretching vibrations of CH and the second to the bending of CH and lastly the stretching vibration of CO, which confirms the interaction of PEG on the surface of TiO$_2$ through the H bond [56]. The peaks at 652 and 596 cm$^{-1}$ are assigned to the lattice vibration of TiO$_2$ (Ti–O–Ti) [57]. In general, deposited-TiO$_2$ materials (Figure 6b) exhibited similar FTIR spectra to pure TiO$_2$; however, the samples exhibited absorption peaks at 2196 and 2341 cm$^{-1}$; this denotes the existence of CO$_2$ molecule in air [58,59].
which presents a slight increase (21.3 m$^2$ g$^{-1}$) in the BET surface area. The results of the N
physisorption analysis agree with the SEM and TEM analyses, maintaining a relationship between the nanometric size of the samples and the specific surface area. The mesoporous structure obtained in the synthesized nanomaterials in this study presented a hysteresis loop for $P/P_0 \sim 0.40$, related to agglomerates of cylindrical pores. On the other hand, the $S_{BET}$ results suggest an increase in adsorption process within the active sites promoted by the interaction between the mesoporous structure and the pore size distribution. Furthermore, the incorporation of metallic ions over TiO$_2$ support contributed to an improvement in the efficiency of the photocatalytic activity.

### 3.6. Nitrogen Physisorption Analysis

Figure 7 shows the adsorption–desorption isotherms of the pure and deposited-TiO$_2$ nanoparticles (M = Co, Cu, Fe, and Ni) and BJH pore size distribution. The deposited materials are classified as Type IV isotherms, associated with the physisorption of mesoporous materials according to IUPAC classification [60]. Moreover, the common characteristic is the hysteresis loops present in the multilayer range of the physisorption isotherms that suggest capillary condensation associated with mesoporous-like structures. The results of pure TiO$_2$ exhibit an H2 type hysteresis loop, which changes to H4 upon deposition of ion metal (Co, Cu, Fe, and Ni) on the surface of the support [48]. These conditions promote the modification of the textural properties of the materials. In Table 1, it can be seen how the volume and average pore size decrease after metal loading. Employing the BJH method, the average pore size was calculated, showing a significant decrement due to the dopant compared to pure TiO$_2$. However, the specific surface areas ($S_{BET}$) did not present significant changes after the deposition–precipitation process, except for Ni/TiO$_2$, which presents a slight increase (21.3 m$^2$ g$^{-1}$). The heterogeneous photocatalysis process depends mainly on a mesoporous structure, a small pore diameter, and a large pore volume, achieving a significant improvement in the photocatalyst activity by decreasing the degree of mass transfer [61]. Alalm et al. reported an enhance in the photocatalytic activity due to high surface area enhanced by incorporation of sulfur cations into the lattice of TiO$_2$ [1]. It has been reported that the specific surface area of TiO$_2$ may be influenced by the presence of different metallic ions (Cu, Co, Ni, Pd, Sn, and Zn) and their concentrations loaded in the support [48]. In this context, the surface composition of the resultant nanomaterial may exhibit changes associated with a good dispersion of the metallic ions on the support [62]. The results of the N$_2$ physisorption analysis agree with the SEM and TEM analyses, maintaining a relationship between the nanometric size of the samples and the specific surface area. The mesoporous structure obtained in the synthesized nanomaterials in this study presented a hysteresis loop for $P/P_0 \sim 0.40$, related to agglomerates of cylindrical pores [63].
3.7. XPS Spectroscopy Analysis

The XPS analysis was carried out for the identification of elements present and the valence states of the TiO$_2$, Co/TiO$_2$, Cu/TiO$_2$, Fe/TiO$_2$ and Ni/TiO$_2$. Figure 8 shows the deconvoluted XPS spectra of the Ti 2p orbital for the TiO$_2$, and the characteristic peaks for Ti 2p$_{3/2}$ were observed at 458.55, and 464.27 eV for Ti$^{4+}$ [65]. After depositing, the nanoparticles show the presence of the valence state Ti$^{3+}$ indicating the formation of Ti$_2$O$_3$ in the nanoparticles, which suggests a development of mixed oxides and TiO$_2$ [66]. The shift in the position of these peaks indicates an influence of ion addition on the electronic state of Ti, and the presence of Ti$^{3+}$ indicates the formation of Ti-O-M structure over the lattice of the support [65]. In the case of deposited nanomaterials Ti$^{4+}$, these peaks were found at 461.04 (Co/TiO$_2$), 459.99 (Cu/TiO$_2$), 458.91 (Fe/TiO$_2$), and 458.06 eV (Ni/TiO$_2$) for Ti 2p$_{3/2}$ and 467.31 (Co/TiO$_2$), 466.43 (Cu/TiO$_2$), 472.01 (Fe/TiO$_2$), and 464.41 eV (Ni/TiO$_2$) for Ti 2p$_{1/2}$. The Ti$^{3+}$ species was located at 458.62, 458.31, 457.72, and 456.88 eV, for Ti 2p$_{3/2}$, respectively. Additionally, the photoelectronic splitting of Ti 2p$_{3/2}$ was located at 465.89, 464.25, 471.57, and 462.85 for Ti$^{3+}$, respectively [65,67]. These results are in agreement with those previously reported in the literature [68–71]. A satellite peak was also observed at 464.21 (Fe/TiO$_2$) and 460.04 (Ni/TiO$_2$) for Ti 2p$_{3/2}$ and 471.96 (TiO$_2$), 474.95 (Co/TiO$_2$), 472.29 (Cu/TiO$_2$), 477.58 (Fe/TiO$_2$), and 469.87 (Ni/TiO$_2$) eV for Ti 2p$_{1/2}$ [72,73].

The different species (Co/TiO$_2$, Cu/TiO$_2$, Fe/TiO$_2$, and Ni/TiO$_2$) are present in Figure 9 as 2p$_{1/2}$ and 2p$_{1/2}$ for nanomaterials. The valence state of Co/TiO$_2$ corresponding to Co 2p$_{3/2}$ are located at 783.71 (Co$^{3+}$) and 780.49 eV (Co$^{2+}$); additionally, the peaks of Co 2p$_{1/2}$ are presented at 799.72 (Co$^{3+}$) and 797.07 eV (Co$^{2+}$) [22]. The Cu/TiO$_2$ NPs presents signals characteristic to Cu 2p$_{3/2}$ at 933.31 (Cu$^+$) and 935.85 eV (Cu$^{2+}$), for Cu 2p$_{1/2}$, the peaks were found at 953.04 (Cu$^+$) and 955.49 eV (Cu$^{2+}$) [46]. In the case of Fe/TiO$_2$, the signals of Fe 2p$_{3/2}$ are located at 710.89 (Fe$^{2+}$) and 712.82 eV (Fe$^{3+}$), 724.70 (Fe$^{2+}$) and 725.98 eV (Fe$^{3+}$) for Fe 2p$_{1/2}$ [22]. The signals of Ni/TiO$_2$ are located at 857.28 and 862.76 eV for Ni 2p$_{3/2}$. On the other hand, the peaks for Ni 2p$_{1/2}$ were located at 874.73 and 881.02 eV [74]. Additional shake-up satellites signals were identified at 788.04 Co$^+$, 804.94 Cu$^+$, 942.83 Cu$^{2+}$, 962.76 Cu$^{3+}$, 718.60 Fe$^+$, 732.84 Fe$^{2+}$, 865.81 Ni$^+$, and 885.59 eV Ni$^{2+}$ are also observed (Figure 9). The identification of parameters of the physic-chemical surface

Figure 7. Nitrogen adsorption-desorption isotherms and the corresponding pore size distribution curves (inset): (a) TiO$_2$, (b) Co/TiO$_2$, (c) Cu/TiO$_2$, (d) Fe/TiO$_2$ and (e) Ni/TiO$_2$. 
provides an idea of the elements in the sample, the chemical state in which they are found, and the identification of defect origins for the oxygen vacancy.

**Figure 8.** Ti 2p XPS spectrum of: (a) TiO$_2$, (b) Co/TiO$_2$, (c) Cu/TiO$_2$, (d) Fe/TiO$_2$ and (e) Ni/TiO$_2$.

**Figure 9.** Higher-resolution deconvoluted XPS spectra of: (a) Co/TiO$_2$, (b) Cu/TiO$_2$, (c) Fe/TiO$_2$ and (d) Ni/TiO$_2$. 

**Figure 10.** Illustrates the XPS spectra of O1s, and TiO$_2$ pure shows a strong signal at 530.76 eV attributed to the crystal lattice oxygen O$_{2-}$ (O-Ti bond) [75]. The deposited samples show the same peak signal at 532.29 (Co/TiO$_2$), 529.59 (Cu/TiO$_2$), 529.96 (Fe/TiO$_2$), and 529.76 eV (Ni/TiO$_2$) [76]. The broad band centered at 529.79, 531.19, 528.75, 528.55, and 528.20 eV that are associated with C=O (oxygen double bond to aromatic carbon) group, respectively [77]. The peaks at about 531.39 (TiO$_2$), 533.00 (Co/TiO$_2$), 530.82 (Cu/TiO$_2$), 531.35 (Fe/TiO$_2$), and 532.11 eV (Ni/TiO$_2$) indicate the presence of C-OH or adsorbed OH$^{-}$ group [78]. The bonds observed at 534.47 (Co/TiO$_2$), 532.61 (Cu/TiO$_2$), 531.84 (Fe/TiO$_2$), and 534.45 eV (Ni/TiO$_2$) correspond to the O-C=O group [78,79]. According to these data, the photocatalysts presented an improvement in the generation of hydroxyl groups, which are essential in photocatalytic applications since they interact with photoinduced holes by promoting the production of hydroxyl radicals on the surface of materials, favoring oxidation reactions during photocatalytic degradation of organic pollutants [64].
Figure 10 illustrates the XPS spectra of O 1s, and TiO$_2$ pure shows a strong signal at 530.76 eV attributed to the crystal lattice oxygen O$^{2-}$ (O-Ti bond) [75]. The deposited samples show the same peak signal at 532.29 (Co/TiO$_2$), 529.59 (Cu/TiO$_2$), 529.96 (Fe/TiO$_2$), and 529.76 eV (Ni/TiO$_2$) [76]. The broad band centered at 529.79, 531.19, 528.75, 528.55, and 528.20 eV that are associated with C=O (oxygen double bond to aromatic carbon) group, respectively [77]. The peaks at about 531.39 (TiO$_2$), 533.00 (Co/TiO$_2$), 530.82 (Cu/TiO$_2$), 531.35 (Fe/TiO$_2$), and 532.11 eV (Ni/TiO$_2$) indicate the presence of C-OH or adsorbed OH$^-$ group [78]. The bonds observed at 534.47 (Co/TiO$_2$), 532.61 (Cu/TiO$_2$), 531.84 (Fe/TiO$_2$), and 534.45 eV (Ni/TiO$_2$) correspond to the O-C=O group [78,79]. According to these data, the photocatalysts presented an improvement in the generation of hydroxyl groups, which are essential in photocatalytic applications since they interact with photoinduced holes by promoting the production of hydroxyl radicals on the surface of materials, favoring oxidation reactions during photocatalytic degradation of organic pollutants [64].

On the other hand, the presence of C in the XPS spectra resulted from the organic compounds used during the deposition–precipitation method, indicating the addition of ions elements during these processes. The principal peak (C-C) of C 1s spectra (Figure 11) shows signals from about 284.77 (TiO$_2$), 285.09 (Co/TiO$_2$), 284.84 (Cu/TiO$_2$), 284.11 (Fe/TiO$_2$), and 285.23 eV (Ni/TiO$_2$). The C 1s shows the C=C chemical state at 283.81, 283.31, 284.05, 283.22, and 283.71 eV, respectively. The C-OH group appears at 285.35 (TiO$_2$) and 285.43 eV (Fe/TiO$_2$). The peaks at 286.09 (Cu/TiO$_2$) and 286.72 eV (Ni/TiO$_2$) correspond to group C-O-O. The peaks assigned at 287.46 (Co/TiO$_2$) and 289.06 (Fe/TiO$_2$) are attributed to group C=O. In addition, peaks at 288.53 (TiO$_2$), 288.75 (Cu/TiO$_2$) and 288.33 eV (Cu/TiO$_2$) were related with group O-C=O. These results are similar with those reported by Feng et al. [80] and Dougherty et al. [78].
3.8. Degradation of Organic Compounds

The photocatalytic activities of TiO$_2$ and modified-TiO$_2$ materials were carried out using 2,4-D and 2,4-DCP organic compounds. These solutions were exposed to UV-light irradiation in the absence and presence of 100 mg L$^{-1}$ of TiO$_2$ and deposited-TiO$_2$ as photocatalysts. Figures 12 and 13 show the evolution of 2,4-D and 2,4-DCP as a function of time ($p < 0.05$). In 2,4-D, the highest degradation was achieved using Ni/TiO$_2$ (85.6% in 360 min) followed by Fe/TiO$_2$ (86.5% in 360 min), TiO$_2$ (70.1% in 360 min), Co/TiO$_2$ (21.8% in 360 min), Cu/TiO$_2$ (16.6% in 360 min), and photolysis (7.8% in 360 min). Siah et al. used TiO$_2$ with Lanthanum at 0.1, 0.5, 1 and 5 mol% in a solution of 50 mL of 2,4-D with 50 mg of catalyst under UV-light (15 mW cm$^{-2}$). They found that the composite La/TiO$_2$ 0.1 mol% obtained a removal percentage reaching 59.8% after 360 min of light irradiation [81]. In another work, a solution with 90 mg L$^{-1}$ of 2,4-D at pH 3 found a conversion of 63% after 300 min of photocatalytic activity under UV-light (1.8 mW cm$^{-2}$) used 600 mg L$^{-1}$ of N-TiO$_2$ and urea (1:0.5 weight ratio) [82].

![Figure 11. C 1s XPS spectrum of: (a) TiO$_2$, (b) Co/TiO$_2$, (c) Cu/TiO$_2$, (d) Fe/TiO$_2$ and (e) Ni/TiO$_2$.](image)

![Figure 12. Degradation activity of 2,4-D (a) and percentage of degradation after 6 h of reaction (b). For the plot (b), all values are mean± standard deviation of three determinations. Different letters in each column indicate significant statistical differences between treatments ($p < 0.05$).](image)
Similar results were found in the 2,4-DCP where the best photocatalytic activity was achieved using Ni/TiO2 (90.3% in 360 min) followed by Fe/TiO2 (86.5% in 360 min), TiO2 (85.7% in 360 min), Cu/TiO2 (74.0% in 360 min), Co/TiO2 (72.2% in 360 min), and photolysis (67.9% in 360 min). In the literature, a 61.6% degradation of 2,4-DCP (40 mg L\(^{-1}\)) was reported when using mixed matrix photocatalytic membranes (MMMs) with Co/TiO2 at 1% (containing 1.34 mol\%-Co). The solution was fed to the membrane module with a flow rate of 1.5 L min\(^{-1}\) at a pressure of 12 bar. After 30 min, the permeate was measured and analyzed. The UV-light source was a 400 W metal halide lamp and photon flux of 510 nm [83]. Moreover, in a solution of 2,4-DCP (250 mg L\(^{-1}\)), using S-TiO2 dose of 800 mg L\(^{-1}\) under visible light irradiation at 400 W (510 nm) after 240 min, a degradation efficiency of 91% was determined [1]. The XPS deconvolution analysis revealed the presence of Ti\(^{3+}\) species, which is directly associated with the presence of oxygen vacancies. The ions’ metallic defects in the samples of deposited-TiO2 promote an enhanced absorption of UV-light by promoting charge separation and electron transfer during photocatalytic activity [47]. Shen et al. suggest that the increase in the photocatalytic activity is directly related to the ability of the catalyst to generate free radicals, which are responsible for giving way to the oxidation and reduction processes [84,85].

3.9. Kinetics of Photocatalytic Degradation

The Langmuir–Hinshelwood model was used to calculate the kinetics of photocatalytic degradation of 2,4-D and 2,4-DCP compounds in solution. The relationship between the rate of degradation \((r)\) and the concentration of organic pollutants \((c)\) was obtained by applying the following equation:

\[
\frac{dc}{dt} = \frac{kKc}{1 + Kc}
\]

where \(k\) is the rate constant, and \(K\) is the adsorption equilibrium constant on the catalyst surface, and \(t\) is the irradiation time (min). If the concentration is less than 1, this equation can be simplified to the following pseudo-first-order kinetics:

\[
\ln \left( \frac{C_0}{C} \right) = kkt = k_{app}t
\]
The apparent first-order rate constant \( k_{\text{app}} \) (min \(^{-1}\)) for the compounds degradation can be expressed by plotting \( \ln(C_0/C) \) versus time \( (t) \). The relation between initial concentrations of pollutants on the \( k_{\text{app}} \) values obtained on the degradation of different concentrations of organic compounds within 360 min is shown in Figure 14.

![Figure 14](image_url)

**Figure 14.** Experimental data and fitting assuming a pseudo-first order reaction rate: 2,4-D (a) and 2,4-DCP (b).

The pseudo-first order reaction rate constant and the half-life or half-time of the reaction, which is the time required to drop the reactant concentration, are presented in the Table 3. The constant rate and half-life of reaction showed better results with the Ni/TiO\(_2\) sample than for the pure TiO\(_2\) catalyst. This result was favored because of the synergy produced between the organic molecules and the metallic ions over TiO\(_2\) surface.

**Table 3.** Rate constant for the pseudo-first order kinetic equation and half-life time for the 2,4-D and 2,4-DCP degradation in the presence of TiO\(_2\) pure and deposited-TiO\(_2\) catalysts.

|       | 2,4-D (min\(^{-1}\)) | t 1/2 (min) | 2,4-DCP (min\(^{-1}\)) | t 1/2 (min) |
|-------|----------------------|-------------|------------------------|-------------|
| Photolysis | 0.0000              | 44,355.80   | 0.0021                 | 698.63      |
| TiO\(_2\) | 0.0019              | 287.68      | 0.0034                 | 154.84      |
| Co/TiO\(_2\) | 0.0002              | 2259.48     | 0.0026                 | 281.43      |
| Cu/TiO\(_2\) | 0.0000              | 2690.36     | 0.0045                 | 157.87      |
| Fe/TiO\(_2\) | 0.0001              | 1257.89     | 0.0049                 | 157.48      |
| Ni/TiO\(_2\) | 0.0037              | 183.71      | 0.0046                 | 49.24       |

The regression coefficient values (\( R^2 \)) of the experiments have been included in Table 4. In addition, different kinds of reaction kinetics models were compared (zero order, first order and the Langmuir–Hinshelwood model) to demonstrate the kinetic degradation. The best model in both cases followed the L-H model that simulates a pseudo-first order kinetics as shown in Table 4.
Table 4. Coefficient of correlation of first-order kinetic equation, coefficient of correlation of zero-order degradation kinetic equation and coefficient of correlation of L-H first-order degradation kinetic equation.

| Compound    | Kinetic Zero Order | Kinetic First Order | Kinetic L-H Model | Kinetic Zero Order | Kinetic First Order | Kinetic L-H Model |
|-------------|--------------------|---------------------|-------------------|--------------------|---------------------|-------------------|
|             | 2,4-D              | 2,4-DCP             |                   |                    |                     |                   |
| Photolysis  | 0.5423             | 0.5423              | 0.8962            | 0.8846             | 0.8838              | 0.9541            |
| TiO₂        | 0.9507             | 0.9509              | 0.9742            | 0.9162             | 0.9154              | 0.9831            |
| Co/TiO₂     | 0.8942             | 0.8941              | 0.9804            | 0.9669             | 0.9679              | 0.9932            |
| Cu/TiO₂     | 0.7989             | 0.7988              | 0.9850            | 0.9471             | 0.9464              | 0.9626            |
| Fe/TiO₂     | 0.9197             | 0.9196              | 0.9783            | 0.9471             | 0.9464              | 0.9932            |
| Ni/TiO₂     | 0.9268             | 0.9256              | 0.9725            | 0.9238             | 0.9222              | 0.9740            |

3.10. Mineralization of Organic Compounds

Figure 15 shows the results of the mineralization of the organic pollutant by analysis of total organic carbon (TOC). An important relationship is observed between the irradiation time of UV-light and the photocatalyst in the mineralization processes. Table 5 shows the percentage of mineralization of TiO₂ and deposited-TiO₂ on the organic compound. The Ni/TiO₂ presented the best efficiency of mineralization by the 2,4-D (68.3%) and 2,4-DCP (86.5%).

![Figure 15. Removal of total organic carbon (TOC): 2,4-D (a) and 2,4-DCP (b).](image_url)

Table 5. Mineralization (%) TOC for 2,4-D and 2,4-DCP.

| Compound | Photolysis | TiO₂  | Co/TiO₂ | Cu/TiO₂ | Fe/TiO₂ | Ni/TiO₂ |
|----------|------------|-------|---------|---------|---------|---------|
| 2,4-D    | 5.3%       | 42.6% | 18.9%   | 19.2%   | 12.4%   | 68.3%   |
| 2,4-DCP  | 53.4%      | 76.8% | 67.2%   | 68.4%   | 73.6%   | 86.5%   |

Table 5 shows the results of the mineralization of the organic pollutant, and the best mineralization is present by Ni/TiO₂ in both cases (68.3% to 2,4-D and 86.5% to 2,4-DCP). This comportment is due to the reduction of band gap of TiO₂, the presence of the O₂ vacancies due to the introduction of the ions metallic over the surface of the support, and the effective separation of e⁻ /h⁺ species in the photocatalyst [13].
3.11. Mechanisms for the Photocatalytic Degradation

Figure 16 shows the photocatalytic mechanisms diagram proposed for the deposited-TiO2 nanomaterials [86]. The photocatalytic process begins when the photocatalysts are excited by UV-light (absorption of a photon) to promote the formation of oxidizing agents (electron-hole pairs) over the surface of the nanoparticle support. The photogenerated electrons in the TiO2 conduction band (CB) react with oxygen dissolving in water molecules forming superoxide anions (-O2\(^{-}\)). Furthermore, the -O2\(^{-}\) interact with water molecules generated by hydroxyl radicals (·OH). Additionally, the holes (h\(^{+}\)) of the valence band (VB) of TiO2 migrate to the VB of the dopant Metals (M); then, its h\(^{+}\) can react with water molecules on the surface to produce a chain of reaction with ·OH [87,88]. The radicals interact directly with the contaminant (2,4-D or 2,4-DCP) from this process, degrading its structure until simple molecules such as CO\(_2\) and H\(_2\)O are obtained [76]. Suggested reactions are listed below (Equations (6)–(11)):

\[
\text{TiO}_2 + \text{hv} \rightarrow \text{TiO}_2 \left( e_{\text{CB}}^- + h_{\text{VB}}^+ \right) \quad (7)
\]
\[
\text{TiO}_2 \left( e_{\text{CB}}^- \right) + \text{O}_2\text{Aq} \rightarrow - \text{O}_2\text{Aq} \quad (8)
\]
\[
- \text{O}_2\text{Aq} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \cdot \text{OH} \quad (9)
\]
\[
\text{M}(h_{\text{VB}}^+) + \text{H}_2\text{O} \rightarrow \text{H}^+ + \cdot \text{OH} \quad (10)
\]
\[
- \text{OH} + 2,4\text{-D} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (11)
\]
\[
- \text{OH} + 2,4\text{-DCP} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (12)
\]

The main objective of the photocatalytic activity is the mineralization of the organic compounds. According to the results and the information reported in the literature, the following degradation pathway was proposed when the samples were analyzed by HPLC MS. The hydroxyl-based decomposition of 2,4-D, 2,4-DCP used ion metallic deposited over TiO2 under UV-light start when the hydroxyl radical attacks the chloride at the ortho and para position formed 2-chloro-4-hydroxyphenol. Subsequently, it begins to decline to form 2-chloro-5-hydroxy-1,4-benzoquinone. In the next stage, hydroxyl radicals interact with the pollutants until being converted to tetrahydroxybenzene. On the other hand, the rupture of the benzene ring (the products are maleic, fumaric, oxalic, formic and acetic acids) favors the formation of different compounds of aliphatic carboxylic acid, which when decomposed gave CO\(_2\) and H\(_2\)O [89–92].

![Figure 16. Photocatalytic mechanisms diagram for the deposited-TiO\(_2\).](image-url)
4. Conclusions

TiO$_2$ nanomaterials were modified from metal ions (Co$^{+}$, Cu$^{+}$, Fe$^{+}$, and Ni$^{+}$ to 5 at. wt.%) by the deposition–precipitation method. The nanoparticles present a semi-spherical, homogeneous, dispersed shape, according to SEM and TEM analyses. The deposition of metallic ions on TiO$_2$ shifted the light absorption towards the visible region. The interaction of the ions on the support does not present significant changes in its structure, conserving the anatase and rutile crystalline phase according to the SAED and XRD results. The FT-IR and XPS results show each element’s characteristic bonds in the modified TiO$_2$ samples. In this sense, the specific surface area of the samples of modified TiO$_2$ presents a slight increase compared to pure TiO$_2$. The defects caused by the metallic ions have favored improving the structural, morphological, optical, and surface properties of the modified TiO$_2$, promoting the improvement of the photocatalytic activity. Among several modified TiO$_2$ materials, Ni/TiO$_2$ shows the highest photocatalytic activity for the degradation of 2,4-D (85.6%) and 2,4-DCP (90.3%), as well as the highest mineralization 2,4-D (68.3%) and 2,4-DCP (86.5%). Ni/TiO$_2$ follows the pseudo-first order Langmuir–Hinshelwood rate constant relationship in photocatalytic degradation reactions.

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