



Removal of Clothianidin from Surface Water Using TiO₂/CNT/Pd-Cu Nanocomposite Under Photocatalytic Conditions

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Abstract In the study, the Clothianidin extracted from surface water of Aegean region in İzmir were photodegraded using TiO₂/CNT/Pd-Cu nanocomposite. The maximum Clothianidin photodegradation rate was observed as 98% at 20 mg/L Clothianidin concentration using 0.12 mg/L TiO₂/CNT/Pd-Cu Nanocomposite. At 40 mg/L Clothianidin concentration the photodegradation yield decreased to 56%. The maximum Clothianidin photodegradation efficiency was found to be 98% at an alkaline pH of 10.00 at a Clothianidin concentration of 20 mg/L using 0.15 mg/L TiO₂/CNT/Pd-Cu nanocomposite concentration after 65 min under solar light irradiation. By the metal composition of TiO₂/CNT/Pd-Cu 68.6 wt% TiO₂ + 29.4 wt% CNT + 1 wt% Pd + 1 wt%; 99.90% Clothianidin photodegradation yield was detected.

Keywords Surface water, Clothianidin, Photodegradation, nanocomposite, endocrine disruptors, Neonicotinoids, TiO₂/CNT/Pd-Cu

1. Introduction

Neonicotinoids are a group of insecticides, following organophosphorus, and carbamates, and developed versus nicotine properties [1]. The neonicotinoids can be used in the world to control of piercing-sucking mouth insects concerning the delphacidae, since their well root charming, and high yields and decreased inhibitions to mammals [2]. Neonicotinoids were effective agonists of the acetylcholine receptors in nicotine. This act an important factor for the nervous of the insects. These insecticides lead to nerve inhibitions and ending by paralysis and death as a result toxic effects to the nerves. With the detection of novel nicotine-relevant organics a lot of insecticide assays were performed to determine metabolic properties of insects [3]. The stability and steady-state conditions and the resistance of neonicotinoids decreased after operating the treatment plants. The photo-removal of neonicotinoids and the effect of some operational conditions were necessary to raising of insecticidal stability. A lot pesticides are stable and resistant to photodegradation depending to physicochemical metabolic differences [4]. During photo-oxidation of pesticides in aquatic ecosystems spraying of a chemical completely changes the genetic properties and exhibited some sustainabilities to their oxidation [5]. The photo-oxidation process two big process were performed; photosensitization and photo-quenching [6]. The photo-oxidation process pathways and formed metabolites varied according to differences in environmental and operational conditions [7]. No more study was found about the photo-oxidation of neonicotinoid chemicals. However in recent years a significant increase in the degradation of these chemicals were performed. In last years the utilization of clothianidin were extremely increased. The natural



structure such as rivers and seas were polluted. It is important to note that presence of the micropollutants raised by the utilization of these chemicals.

Micropollutants are pollutants, with low level of concentrations such as ng/L and $\mu\text{g/L}$ [1]. Clothianidin was measured in Minnesota ground water and surface water at levels below the guidance value developed by The Minnesota Department of Health. Drinking water is exactly the point emitted to the clothianidin. In some researches, high doses of clothianidin cause changes in weight, growth and metabolic activities in animals. 11% of clothianidin was measured in groundwater. In surface water, clothianidin was measured at a concentration as high as 0.26 ppb. The levels and variations of clothianidin depend to the seasons in Minnesota. It was found that in the animals the exposure concentration to clothianidin was found to 100-fold higher in pregnant rats. The female animals also were sensitive to clothianidin. This chemical inhibits the endocrine homeostasis of the human body, and it was measured in the blood and urine. Clothianidin emitted to the lands an aquatic body and degrade neonicotinoid insecticides. Since neonicotinoids, as a part of insecticides, can be adsorbed fully to the plants via root. They are applied to the soil as seed dressing [8]. Researchers showed that 90% of the neonicotinoids used in seed dressings and adsorbed to the soil [9]. There are seven types of neonicotinoids namely imidacloprid, clothianidin, thiamethoxam, dinotefuran, acetamiprid, thiacloprid, and nitenpyram. Imidacloprid is extensively used, add a clothianidin follow it [10]. With the isolation of clothianidin and thiamethoxam in 1991 they used extensively since their physicochemical properties, effective rate, resistance and a special integration to pesticide inhibition [11]. The data having the accumulation, oxidation and degradation in lands were studied. The removal yield of a pollutant in lands is feasible to detect their degradation. The transformation rates of endocrine disruptors varied with environmental conditions, their concentration and accumulation duration [12]. Due to their huge biological talent and chronic inhibition [12], they not be found in receiving waters. Many novel processes were applied to decrease the pollution. Advanced oxidation processes (AOPs) were extensively used to oxidated the neonicotinoids, steroids and other non-degradable chemicals to broken down the recalcitrant groups [13]. Advanced treatment process consists of ozonation, sonication electro-fenton process as photodegradation process [14]. Photocatalytic processes were extensively utilized since it was easily utilized; the oxidative radicals can be easily reduced, due to ultimate mineralization, no sludge generation and high efficiency rate of pollutants [14]. The photodegradation mechanism contained a semiconductor catalyst, under lighth to create a high photodegradation yield. Some researcher's have generated TiO_2 nanocomposite consisting of TiO_2 , and Carbone nanotubes developed from graphene, and some heavy metals [15]. This phenomenon was occurred as follows: (a) TiO_2 photodegradation, (b) an excellent electron-capture property for maximum sorption rate of the organic substances [16] and (c) the improved of the effect of the metal doping to TiO_2 [13]. The physical mixture the TiO_2 , carbonaceous organic substance and heavy metal exhibited an excellent yield in the photo oxidations of chemicals due to a special structure of the nanocatalyst [15]. In the production of the nanocatalyst the noble metals were not so cheap. Therefore, nowadays low- cost new photocatalysts were [17]. Among heavy metals, Cu advice to increase the photooxidation rate of TiO_2 photocatalyst to get the electrons on its surface for adsorption [17]. Therefore, developing of a TiO_2 nanocomposite including the TiO_2 , the carbon nanotube and copper should be a good idea for photocatalysis of pollutants. The photooxidation yield of this new nanocomposite can be improved by doping of a new metal due to mixing of the metals improved the photocatalytic oxidation by a combined effect bigger than that of one metal [17]. In the developing of a new, advanced nanocomposite including the Cu, the Pd, the TiO_2 and the caron nanotube; Pd increase the light absorption; and Cu is working as an electron sink [15]. Therefore, the combination of these ingredients should cause excellent photocatalytic rates in the clothianidin yields.

In order to remove the clothianidin which one of the neonicotinoids from the surface water; $\text{TiO}_2/\text{CNT}/\text{Pd}-\text{Cu}$ nanocomposite was generated under laboratory conditions. The effects of increasing initial clothianidin concentrations (5 mg/L, to 10 mg/L, 20 mg/L and 40 mg/L); effect of pH increase (4.0; 7.0, 8.5 and 10.0), effects of increasing UV-vis spectra wave lengths (300 nm, 400 nm, 500 nm, 600 nm and 700 nm) on the absorbances of $\text{TiO}_2/\text{CNT}/\text{Pd}-\text{Cu} > \text{TiO}_2/\text{CNT}/\text{Pd} > \text{TiO}_2/\text{CNT}/\text{Cu} > \text{TiO}_2/\text{CNT}$, effects of variations of metal percentages of the $\text{TiO}_2/\text{CNT}/\text{Pd}-\text{Cu}$ nanocomposite such as TiO_2/CNT 70 wt% $\text{TiO}_2 + 30$ wt% CNT, $\text{TiO}_2/\text{CNT}/\text{Pd}$ 68.6 wt% $\text{TiO}_2 + 29.4$ wt% CNT + 2 wt% Pd, $\text{TiO}_2/\text{CNT}/\text{Cu}$ 68.6 wt% $\text{TiO}_2 + 29.4$ wt% CNT + 2 wt% Cu, $\text{TiO}_2/\text{CNT}/\text{Pd}-\text{Cu}$ 68.6



wt% TiO₂ + 29.4 wt% CNT + 1 wt% Pd + 1 wt%, on the photodegradation yields of Clothianidin were investigated. Furthermore, in order to detect the surface properties of TiO₂/CNT/Pd-Cu nanocomposite XRD and XPS analysis were performed.

2. Materials and methods

2.1. Used Chemicals in this study

Titanium (IV) isopropoxide, Cu (II) acetylacetonate (99.9%) and Pd (II) acetylacetonate (99%) were included in the process as metal precursors and Titania for photocatalyst synthesis.

All chemicals were purchased from Merck Co. Darmstadt-Germany. Multi-walled carbon nanotubes (98%) as TiO₂ support and pure ethanol as hydrolytic agent has been studied using

and these were obtained from Merck Co. The diameters of the CNT were 12-32 nm (outer) and 4-11 nm (inner) (manufacturer's data), and the BET layer area was 210 m²/g (data not shown). Carbon dioxide (99.9%) was used in the synthesis of the catalyst, which was used as a dissolvent and obtained from Sigma-Aldrich.

Commercial TiO₂ P25 supplied by Sigma-Aldrich was used as the reference photocatalyst. Carbon dioxide (99.9%) was used in the synthesis of the catalyst, which was used as a dissolvent and obtained from Sigma-Aldrich.

The photocatalytic capacity was approved in the disruption of clothianidin (≥ 98%). All purchased from Merck Co. Tert-butyl alcohol (99.5%), p-benzoquinone (99%), sodium azide (99%) and glycerol (99%) were used as radical scavenging chemicals, the chemicals were supplied by Merck Co. H₃PO₄ (85%) and NaOH (98%), supplied by Merck, were used to regulate the pH of the hydrated mixtures if essential. Other dissolvents used were methanol and acetonitrile, both with the maximum pure (HPLC-rate) and supplied from Sigma-Aldrich.

2.2. Preparation of TiO₂/CNT/Pd-Cu Nanocomposite

Synthesis situations were depend on those firstly recorded in literature [18]: pressure 20 MPa, temperature 300 °C, reaction time 2 h, 5 mmol of titanium isopropoxide, 128.4 mg of CNT, molar rates of TIP/ethanol and ethanol/CO₂ equal to 3.6% and 8%, in order of, and volumes of metal first minerals (Pd(II) acetylacetonate or Cu(II) acetylacetonate) lead to composites with metallic weight percent of 2%. To measure the essential volume of CNT it was taken notice that only 75% of titanium available in TIP was incorporated to the photocatalyst [18].

2.3. Clothianidin properties

The clothianidin (C₆N₅H₈SO₂Cl) used in the study were produced by PESTANAL[®], analytical standard MERCK (Figure 1). They were both in dust shape with pure of 99.5%. Present mixture of 1000 mg/L was prepared by solving clothianidin in analytical grade methanol.

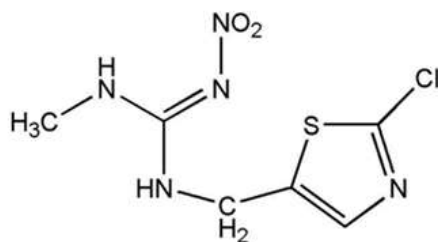


Figure 1: Chemical structure of Clothianidin

2.4. Variation of ingredient percentages in TiO₂/CNT/Pd-Cu Nanocomposite on the photooxidation of Clothianidin

Concerning the volumes required of Pd and/or Cu first minerals, we supposed that 100% of the metal in the first mineral was combined into the photocatalyst. Based on this assumption the composition was arranged as follow:

TiO₂/CNT 70 wt% TiO₂ + 30 wt% CNT

TiO₂/CNT/Pd 68.6 wt% TiO₂ + 29.4 wt% CNT + 2 wt% Pd

TiO₂/CNT/Cu 68.6 wt% TiO₂ + 29.4 wt% CNT + 2 wt% Cu



TiO₂/CNT/Pd-Cu 68.6 wt% TiO₂ + 29.4 wt% CNT + 1 wt% Pd + 1 wt%

The effects of the aforementioned ratios on photodegradation yields of Clothianidin was researched.

2.5. Photocatalytic oxidation tests

The photocatalytic motion of the TiO₂/CNT/Pd-Cu Nanocomposite was researched for the photooxidation of the Clothianidin under irradiation. The photooxidation assays were carried out in a 800 mL glass reactors under mechanical stirring at a pH of 9.0. For light a Xe arc lamp (590 W) was used for a light power of 120 mW. The TiO₂/CNT/Pd-Cu dose was 0.12 g/L and Clothianidin dose at the beginning of the study was 20 mg/L. The TiO₂/CNT/Pd-Cu was put to a glass beaker with Clothianidin at pHs 4.0; 8.5 and 10.0. Then, the surface waters samples from the different points of surface water in around Tahtalı region was provided under mixing in the dark until steady-state conditions were obtained (15 min). In the relevant assay the photocatalytic essay was performed for 150 min under sun light. The data obtained from the photooxidations assays exhibited the arithmetic mean in triplicate studies. Samples of about 2 mL were taken from the glass beakers filtered with an filter apparatus having 0.45 μm membrane filters.

2.6. Measurement of clothianidin

Different clothianidin concentrations (5 mg/L, to 10 mg/L, 20 mg/L and 40 mg/L) were carried out by using methanol. The samples were photo-oxidated under light irradiation, and the samples were retained under dark for control. The mixtures were filtered from the membrane with a membrane filter apparatus having a por diameter of 0.21 μm. The samples were measured in a LC-Q-TOF-MS accoutered with diode array detection. This contains an automatic jet stream electrospray ionization apparatus. The typical ion source properties were: capillary voltage, +4040/-3570 V; temperature, 320°C; gas flow ratio, 7 L/min; case gas temperature, 258°C; sheath gas flow rate, 13 L/min; and nebulizer pressure was 48 psi.

2.7. Physicochemical properties of TiO₂/CNT/Pd-Cu nanocomposite

The physicochemical properties of the TiO₂/CNT/Pd-Cu nanocomposite were determined using X-ray powder diffractometer (XRD, Philips X'Pert MPD). Layer analysis was achieved by the X-ray Photoelectron Spectroscopy (XPS) technique using a spectrometer Specs hoibos-150.

2.8. Effect of pH

The pH has a important effect on the photo-degradation of organic contaminants [19]. In this research, diluted NaOH and HCL were used to obtain pH values of 4.0, 7.0, 8.5, and 10.0 in order to investigate pH effects on the photo-degradation of Clothianidin.

2.9. Effect of the initial Clothianidin concentration on photo-degradation

In order to detect the effect of initial Clothianidin concentrations on photodegradation the Clothianidin concentrations was increased from 5 mg/L, to 10 mg/L, to 20 mg/L and to 40 mg/L.

2.10. Light absorption, charge separation and charge transfer

Diffuse reflectance ultraviolet-visible spectrophotometry (DRS UV-vis) was used to determine the optical specifications of synthesized catalysts.

2.11. Photo-degradation efficiency of Clothianidin

The photo-degradation efficiency was determined from Equation 1:

$$\text{Photodegradation rate (\%)} = \frac{C_d - C_1}{C_d} \times 100 \quad (1)$$

Where; C_d and C₁ are Clothianidin concentrations (darkness control) and different experiments, respectively.



3. Results and Discussion

3.1. Effect of the initial Clothianidin concentration on photo-degradation in the presence of 0.12 mg/L TiO₂/CNT/Pd-Cu Nanocomposite

The recent studies showed that TiO₂/CNT/Pd-Cu Nanocomposite was used to degrade the at Clothianidin concentrations varying between 0.10 and 1.20 mg/L [20]. Therefore, in this step a constant TiO₂/CNT/Pd-Cu Nanocomposite concentration of 0.12 mg/L was used. Table 1 illustrates the photo-oxidation yields of Clothianidin. As the Clothianidin concentrations increased from 5 mg/L, to 10 mg/L, and to 20 mg/L, the photodegradation yields increased from 67% to 80% and 98%. However the yield decreased to 56% at 40 mg/L Clothianidin concentration after 120 min. Excess Clothianidin concentrations at the beginning is relevant to a big part of Clothianidin samples; This is due to high competition between photon absorption and a small amount of energy sorbed by the TiO₂/CNT/Pd-Cu nanocomposite. As a result, small photo-oxidation yields were detected [21]. Furthermore, a lot of metabolites compete for light photons, resulting in low photon adsorptions and reduced photooxidations [22].

Table 1: Effect of increasing initial Clothianidin concentration on photo-degradation

Clothianidin concentration (mg/L)	Photodegradation yield (%)
5	67
10	80
20	98
40	56

3.2. Effect of pH on photodegradation of 20 mg/L Clothianidin in the presence of 0.12 mg/L TiO₂/CNT/Pd-Cu Nanocomposite after 95 min

As shown in Table 2, the photo-oxidation yields decreased under acidic conditions, while the photo-oxidation yields elevated under neutral and alkaline conditions. At pH 4.0, the photo-oxidation yield of Clothianidin was found to be very low. The photo-oxidation yield of Clothianidin elevated at raised pHs, The yield raised at pH 8.5 and 10.0. Neonicotinoids easily generated hydroxyl anions in alkaline conditions in the comparison of the other pH levels. The production of the aforementioned radicals was significantly affect the photo-oxidation yields of Clothianidin [23]. Under acidic conditions the photons were absorbed at a wavelength of 260 nm. This wavelength was the upper sorption wavelength of Clothianidin. As a result, photons compete during the sorption of the photo-oxidation process.

This phenomenon ending with decreased photo-oxidation yields [24]. Under alkaline conditions, an elevated level in photo-oxidation yields depends to an elevated photo-quantum efficiency. This cause to raise of the protonation degree of the excited Clothianidin [25].

Table 2: Effect of increasing pH on the photodegradation of Clothianidin

pH level	Clothianidin Photodegradation yield (%)
4	60
7	67
8.5	87
10	99.90

3.3. Photocatalytic studies with 20 mg/L Clothianidin at pH=10.0 and at a initial 0.15 mg/L TiO₂/CNT/Pd-Cu Nanocomposite dose after 120 min

Table 3 shows the Clothianidin photodegradation yield under optimal conditions. With the aforementioned doses 99.99% Clothianidin yields was detected.

Table 3: Effect optimal operational conditions on the photodegradation of Clothianidin

pH level	Clothianidin concentration (mg/L)	TiO ₂ /CNT/Pd-Cu dose (mg/L)	Clothianidin Photodegradation yield (%)
10	20	0.15	99.99



3.4. Effects of metal percentages in TiO₂/CNT/Pd-Cu nanocomposite on photodegradation of Clothianidin

Table 4 exhibited the photodegradation yields of 20 mg/L Clothianidin with 0.15 mg/L total TiO₂/CNT/Pd-Cu with different TiO₂, CNT, Pd, and Cu percentages

Table 4: Effects of metal percentages in TiO₂/CNT/Pd-Cu nanocomposite on photodegradation of Clothianidin

Variation of metal percentages in the TiO ₂ /CNT/Pd-Cu	Clothianidin Photodegradation yield (%)
TiO ₂ /CNT 70 wt% TiO ₂ + 30 wt% CNT	77
TiO ₂ /CNT/Pd 68.6 wt% TiO ₂ + 29.4 wt% CNT + 2 wt% Pd	80
TiO ₂ /CNT/Cu 68.6 wt% TiO ₂ + 29.4 wt% CNT + 2 wt% Cu	81
TiO ₂ /CNT/Pd-Cu 68.6 wt% TiO ₂ + 29.4 wt% CNT + 1 wt% Pd + 1 wt% Cu	99.99

The results showed that the maximum Clothianidin Photodegradation yield was detected with TiO₂/CNT/Pd-Cu 68.6 wt% TiO₂ + 29.4 wt% CNT + 1 wt% Pd + 1 wt% containing all types of metals in the formation of TiO₂/CNT/Pd-Cu nanocatalyst.

3.5. Photodegradation kinetic of Clothianidin

TiO₂/CNT/ Pd-Cu nanocomposite exhibited a huge Clothianidin yield as illustrated in Figure 2. Clothianidin level decreased after 120, 50 and 30 min of photooxidation. The TiO₂/CNT/Pd-Cu nanocomposite exhibited excellent removals for Clothianidin after 150, 90 and 60 min photooxidation times. When the TiO₂/CNT/Pd-Cu composites were without all its ingredients exhibited reduced photooxidation yields. For TiO₂/CNT/Pd-Cu nanocomposite the lowest time for maximum Clothianidin yield was found to be as 65 min. Although high removal yields was found for Clothianidin in the presence of a lowest part of this chemical indicated that some metabolites at insignificant levels were found.

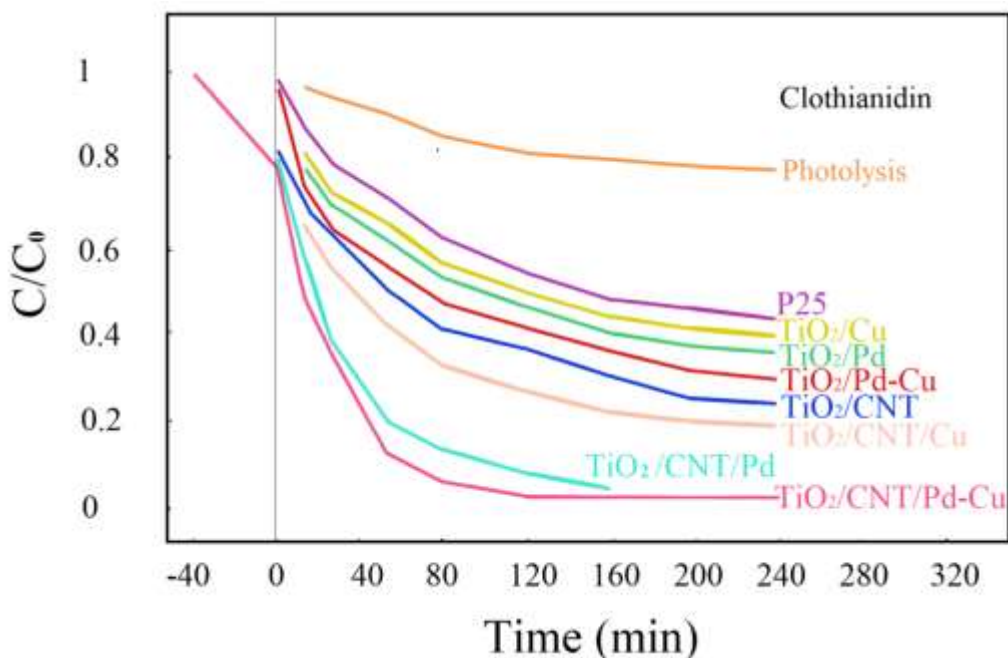


Figure 2: Photodegradation of clothianidin under simulated solar light

3.6. Light absorption, charge separation and charge transfer

Figure 3 exhibited the presence of TiO₂ P25 in the wavelengths range from 302 to 702 nm. The sorption spectra of UV region showed that of the absorption spectrum exhibited that TiO₂ was not hybrid, it was found solely and the UV-vis spectra exhibited the presence of TiO₂ metal. The absorption lines showed that TiO₂ mainly absorbed in the UV region at wave lengths < 300 nm. The spectra of the nanocomposites in the visible light area is as follows:



$\text{TiO}_2/\text{CNT}/\text{Pd-Cu} > \text{TiO}_2/\text{CNT}/\text{Pd} > \text{TiO}_2/\text{CNT}/\text{Cu} > \text{TiO}_2/\text{CNT}$. The properties of the Ti–O–C bonds generated in each was completely different [26]. In the hybrid nanocomposite, absorption of visible light occurred extensively since Ti-O-C bonds cause to photon charge and Transmittance of the photons between TiO_2 and carbon nanotubes This situation decrease the recombination. Plasmonic Pd interaction with visible light and the formation of Schottky junctions by producing new energies between Pd and Cu near conduction band of TiO_2 [27].

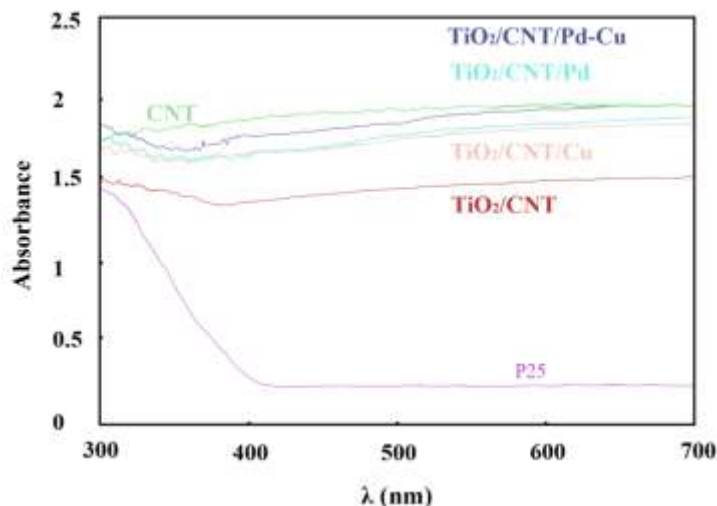


Figure 3: UV-vis DRS spectra of the photocatalysts

3.7. Physicochemical properties of Pd-Cu/20 CNT TiO_2 nanocomposite

3.7.1. XRD analysis

XRD patterns of CNT, Pd-Cu/ TiO_2 , and Pd-Cu/20 CNT TiO_2 were illustrated in Figure 4. Typical (002) and (101) diffraction plots showed the XRD plots of CNT. XRD analysis of TiO_2 and CNT- TiO_2 nanocomposite showed that solely anatase phase was detected in the TiO_2 structure and in whole nano-composit. The XRD pathways of the Pd-Cu doped CNT- TiO_2 were found to be the same to the one of Pd-Cu/ TiO_2 . The CNT was clearly detected.

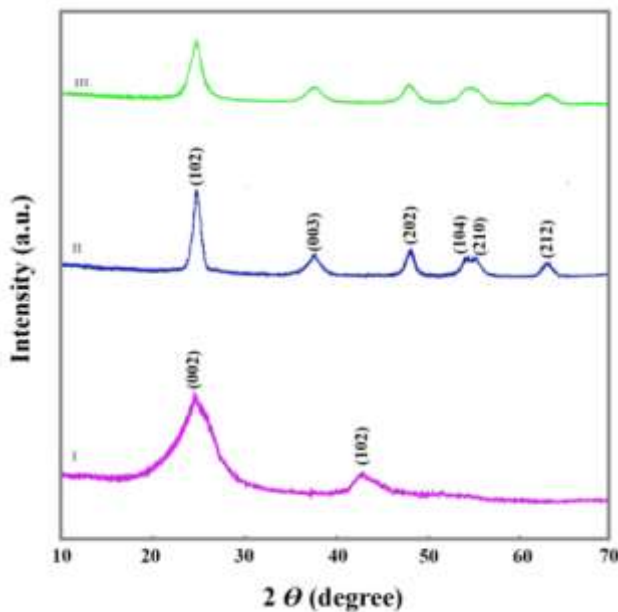


Figure 4: X-ray diffraction patterns of neat CNT (I), Pd-Cu/ TiO_2 (II), and Pd-Cu/20CNT- TiO_2 (III)



3.7.2. XPS analysis

The whole spectrum of TiO₂/CNT/Cu-Pd in the surface illustrated the presence of Ti, O, C, Cu and Pd, with photoelectron distributions at binding energies of 284.5 eV (C 1s), 337 eV (Pd 3d), 458.6 eV (Ti 2p), 530 eV (O 1s) and 933 eV (Cu 2p) (data not shown). The Ti 2p high-resolution XPS plot indicated the peaks centered at 458.9 eV and 464.7 eV which these can be correlated with Ti 2p_{3/2} and Ti 2p_{1/2} spin-orbital splitting photoelectrons in Ti⁴⁺, respectively (Figure 5). This showed the occurrence of copper and palladium oxides on the bimetallic on TiO₂/CNT/Cu-Pd nanocatalyst. This showed the generation of excess Schottky barriers at the oxidated TiO₂ surface pores. This provides the formation of charge carriers relevant to TiO₂/CNT/Cu-Pd nano catalyst. The synergistic correlation between TiO₂, CNT, Cu and Pd exhibited the excellent performance of the TiO₂/CNT/Cu-Pd catalyst during photooxidation.

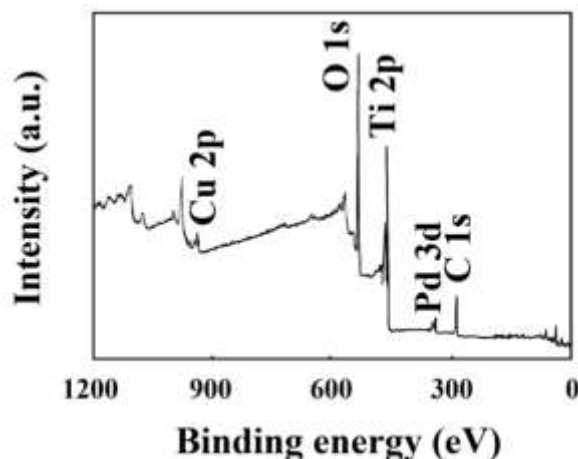


Figure 5. XPS analysis results

4. Conclusions

With the synthesis of TiO₂/CNT/Pd-Cu nanocomposite Clothianidin was photodegraded with high yields from surface water. The XPS and XRD studies exhibited that the Pd and the Cu ions incorporated into the TiO₂ crystalline with doping of TiO₂ catalyst adsorbed to the CNT surface. For maximum Clothianidin yield (98%) the optimal conditions were pH = 10.00, Clothianidin dose was 20 mg/L, TiO₂/CNT/Pd-Cu nanocomposite dose was 0.15 mg/L, irradiation time was 65 min under solar light irradiation. By the metal composition of TiO₂/CNT/Pd-Cu 68.6 wt% TiO₂ + 29.4 wt% CNT + 1 wt% Pd + 1 wt%; 99.90% Clothianidin photodegradation yield was detected. XRD and XPS analysis qualified the presence of copper and palladium oxides in the TiO₂/CNT/Pd-Cu nanocomposite.

References

- [1]. Finnegan MC, Baxter LR, Maul JD, Hanson ML, Hoekstra PF. Comprehensive Characterization of the Acute and Chronic Toxicity of the Neonicotinoid Insecticide Thiamethoxam to a Suite of Aquatic Primary Producers, Invertebrates, and Fish. *Environ Toxicol Chem.* 2017; 36: 2838–2848. <https://doi.org/10.1002/etc.3846> PMID: 28493485
- [2]. Leiva JA, Nkedikizza P, Morgan KT, Kadyampakeni DM. Imidacloprid Transport and Sorption Nonequilibrium in Single and Multilayered Columns of Immokalee Fine Sand. *PLoS One.* 2017; 12: e0183767. <https://doi.org/10.1371/journal.pone.0183767> PMID: 28837702
- [3]. Yu N, Liu Y, Wang X, Li j, Bao HB, Liu ZW. Heterologous Formation of Neonicotinoid-sensitive nAChRs Containing UNC-38 and UNC-29 Subunits from *Bursaphelenchus xylophilus*. *Pestic Biochem Phys.* 2017; 143: 168–172
- [4]. Azenha ME, Romeiro A, Sarakha M. Photodegradation of Pesticides and Photocatalysis in the Treatment of Water and Waste. *Applied Photochemistry.* 2013; 247–266.



- [5]. Wu SP, Schwab J, Yang BY, Yuan CS. Effect of Phenolic Compounds on Photodegradation of anthracene and Benzo[a]Anthracene in Media of Different Polarity. *J Photoch Photobio A*. 2015; 309: 55–64.
- [6]. Hintz H, Egelhaaf HJ, Lu'er L, Hauch J, Peisert H, Chasse´ T. Photodegradation of P3HT-A Systematic Study of Environmental Factors. *Chem Mater*. 2016; 23: 145–154.
- [7]. Richardson SD, Kimura SY (2016) Water analysis: emerging contaminants and current issues. *Anal Chem* 88:546–582
- [8]. Bonmatin JM, Giorio C, Girolami V, Goulson D, Kreutzweiser DP, Krupke C, Liess M, Long E, Marzaro M, Mitchell EAD, Noome DA, Simon-Delso N, Tapparo A (2015) Environmental fate and exposure; neonicotinoids and fipronil. *Environ Sci Pollut Res* 22(1):35–67
- [9]. Goulson D (2013) An overview of the environmental risks posed by neonicotinoid insecticides. *J Appl Ecol* 50:977–987
- [10]. Cresswell JE, Robert FXL, Florance H, Smirnoff N (2014) Clearance of ingested neo-nicotinoid pesticide (imidacloprid) in honey bees (*Apis mellifera*) and bumblebees (*Bombus terrestris*). *Pest Manag Sci*. 70(2):332–337
- [11]. Zhao Q, GeY, Zuo P, Shi D, Jia S (2016) Degradation of thiamethoxamin aqueous solution by ozonation: influencing factors, intermediates, degradation mechanism and toxicity assessment. *Chemosphere* 146:105–112
- [12]. Yilmaz B., H. Terekeci, S. Sandal, F. Kelestimur, Endocrine disrupting chemicals: exposure, effects on human health, mechanism of action, models for testing and strategies for prevention, *Rev. Endocr. Metab. Disord.* 21 (2020) 127–147, <https://doi.org/10.1007/s11154-019-09521-z>.
- [13]. Misra M., S.R. Chowdhury, T.I. Lee, Sunlight driven decomposition of toxic organic compound, coumarin, p-nitrophenol and photo reduction of Cr(VI) ions, using a bridge structure of Au@CNT@TiO₂ nanocomposite, *Appl. Catal. B: Environ.* 272 (2020), 118991, <https://doi.org/10.1016/j.apcatb.2020.118991>.
- [14]. Tamaddon F., M.H. Mosslemin, A. Asadipour, M.A. Gharaghani, A. Nasiri, Microwave-assisted preparation of ZnFe₂O₄@methyl cellulose as a new nanobiomagnetic photocatalyst for photodegradation of metronidazole, *Int. J. Biol. Macromol.* 154 (2020) 1036–1049, <https://doi.org/10.1016/j.ijbiomac.2020.03.069>.
- [15]. de la Flor M.P., R. Camarillo, F. Martínez, C. Jim´enez, R. Quiles, J. Rinc´on, Synthesis and characterization of TiO₂/CNT/Pd: an effective sunlight photocatalyst for neonicotinoids degradation, *J. Environ. Chem. Eng.* 9 (2021), 106278, <https://doi.org/10.1016/j.jece.2021.106278>.
- [16]. Wang H., X. Liu, P. Niu, S. Wang, J. Shi, L. Li, Porous two-dimensional materials for photocatalytic and electrocatalytic applications, *Matter* 2 (2020) 1377–1413, <https://doi.org/10.1016/j.matt.2020.04.002>.
- [17]. Feng J., X. Zhang, G. Zhang, J. Li, W. Song, Z. Xu, Improved photocatalytic conversion of high-concentration ammonia in water by low-cost Cu/TiO₂ and its mechanism study, *Chemosphere* 274 (2021), 129689, <https://doi.org/10.1016/j.chemosphere.2021.129689>.
- [18]. Rodríguez V., R. Camarillo, F. Martínez, C. Jim´enez, J. Rinc´on, CO₂ photocatalytic reduction with CNT/TiO₂ based nanocomposites prepared by high-pressure technology, *J. Supercrit. Fluids* 163 (2020), 104876, <https://doi.org/10.1016/j.supflu.2020.104876>.
- [19]. Wei ZS, Spinney R, Ke RH, Yang ZH, Xiao RY. Effect of pH on the Sonochemical Degradation of Organic Pollutants. *Environ Chem Lett*. 2016; 14: 163–182.
- [20]. de la Flor María Patricia, Rafael Camarillo, Fabiola Martínez, Carlos Jimenez, Rafael Quiles, Jesusa Rincon., Synthesis and characterization of bimetallic TiO₂/CNT/Pd-Cu for efficient remediation of endocrine disruptors under solar light., *J. Environ. Chem. Eng.* 2022; 10:(2) 107245 <https://doi.org/10.1016/j.jece.2022.107245>
- [21]. Bao YP, Niu JF. Photochemical Transformation of Tetrabromobisphenol A under Simulated Sunlight Irradiation: Kinetics, Mechanism and Influencing Factors. *Chemosphere*. 2015; 134: 550–556. <https://doi.org/10.1016/j.chemosphere.2014.12.016> PMID: 25559172



- [22]. Basley K, Goulson D. Neonicotinoids Thiamethoxam and Clothianidin Adversely Affect the Colonisation of Invertebrate Populations in Aquatic Microcosms. *Environ Sci Pollut R*. 2018; 25: 9593–9599.
- [23]. Miao J, Sunarso J, Su C, Zhou W, Wang SB, Shao ZP. SrCo_{1-x}Ti_xO_{3-δ} Perovskites as Excellent Catalysts for Fast Degradation of Water Contaminants in Neutral and Alkaline Solutions. *Sci Rep*. 2017; 7:44215. <https://doi.org/10.1038/srep44215> PMID: 28281656
- [24]. Vorobey P, Steindal AE, Off MK, Vorobey A, Moan JE. Influence of Human Serum Albumin on Photodegradation of Folic Acid in Solution. *Photochem Photobiol*. 2010; 82: 817–822.
- [25]. Batchu SR, Panditi VR, O’Shea KE, Gardinali PR. Photodegradation of Sulfonamide Antibiotics in Simulated and Natural Sunlight: Implications for Their Environmental Fate. *J Environ Sci Heal B*. 2014; 49: 299–310.
- [26]. Abega A.V., H.M. Ngomo, I. Nongwe, H.E. Mukaya, P.M.A.K. Sone, X.Y. Mbianda, Ti³⁺ ions and application in the photocatalytic degradation of organic contaminants in water, *Synth. Met*. 251 (2019) 1–14, <https://doi.org/10.1016/j.synthmet.2019.03.012>.
- [27]. Larrosa P., S. Dunn, Photoelectrocatalysis of Rhodamine B and solar hydrogen production by TiO₂ and Pd/TiO₂ catalyst systems, *Electrochim. Acta* 231 (2017) 641–649, <https://doi.org/10.1016/j.electacta.2017.02.035>.

