

Article

TiO₂-Fly Ash Composites for Photocatalytic Degradation of Organic Loading from Real Municipal Wastewater

Mirela Alina Constantin ¹, Ioana Alexandra Ionescu ¹, Florenta Daniela Constantinov ¹,
Cristina Mihaela Nicolescu ², Marius Bumbac ², Anca Irina Gheboianu ³
and Lucian Alexandru Constantin ^{1,*}

- ¹ National Research and Development Institute for Industrial Ecology-ECOIND, 57–73 Drumul Podu Dambovitei Street, 060652 Bucharest, Romania; alina.constantin@incdecoind.ro (M.A.C.); ioana.ionescu@incdecoind.ro (I.A.I.); daniela.constantinov@ecoind.ro (F.D.C.)
² Faculty of Science and Arts, Valahia University of Targoviste, 13 Sinaia Alley, 130004 Targoviste, Romania; cristina.nicolescu@valahia.ro (C.M.N.); marius.bumbac@valahia.ro (M.B.)
³ Institute of Multidisciplinary Research for Science and Technology, Valahia University of Targoviste, 13 Sinaia Alley, 130004 Targoviste, Romania; anca.gheboianu@valahia.ro
* Correspondence: lucian.constantin@incdecoind.ro

Abstract

Fly ash-TiO₂ composites were obtained by sol–gel, and their catalytic performance was evaluated on removal of organic loading and expressed as Chemical Oxygen Demand (COD) from real wastewater samples. SEM, X-ray fluorescence, XRD, IR, Raman analysis and determination of PZC characterized the catalysts. The photocatalytic tests were carried out in a laboratory reactor under UV-VIS irradiation and influence of fly ash (FA) content, and irradiation time was investigated. The catalysts with FA content of 10%, 20% and 30% showed COD removal efficiencies higher than 50% after 5 h of irradiation. The COD degradation followed a pseudo-first order kinetic model. Obtained results proved that FA-TiO₂ composites could represent a suitable alternative for removal of organic loading from real wastewater.

Keywords: fly ash; TiO₂; wastewater; UV light; chemical oxygen demand

1. Introduction

Water scarcity is becoming an increasingly critical issue worldwide due to population growth and climate change, compelling societies to adapt to reduced water availability. While industrial manufacturing is a major consumer of clean water, there has been minimal water recycling in this sector. This is particularly notable in industries where wastewater often contains only mild contamination from dissolved organic compounds [1]. Research into advanced titanium dioxide (TiO₂)-based materials continues to accelerate, driven primarily by environmental applications, especially in water purification and treatment—a persistent global challenge. While pure TiO₂ is recognized as one of the premier semiconductor photocatalysts due to its chemical stability, light sensitivity, and minimal toxicity, scientists remain committed to developing even more effective TiO₂-based photocatalytic materials [2].

TiO₂ photocatalysis continues to face challenges as modern applications demand materials with balanced, multifunctional properties. Consequently, understanding how various TiO₂ characteristics affect its photocatalytic efficiency remains a significant research focus. The scientific literature [3] reports numerous strategies to address TiO₂'s inherent



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limitations, including extending its spectral response range and improving light utilization through various structural approaches. Heterogeneous photocatalysis offers a promising alternative to traditional methods of degrading Dissolved Organic Compounds treatment since it may fully mineralize hazardous pollutants without creating secondary contamination [4]. TiO_2 is commonly considered an n-type semiconductor with a bandgap (E_g) for anatase = 3.2 eV and for rutile = 3.0 eV and limits its absorption to only the ultraviolet part of sunlight (less than 5%). The high photogenerated electron–hole recombination rate of TiO_2 materials leads to low quantum efficiency. Improving the quantum efficiency and photocatalytic activity has always been a concern in the field of photocatalysis [5].

The transformation of compounds depends on their adsorption tendency to the catalyst, with hydroxyl radicals ($\text{HO}^\bullet$) primarily responsible for compounds with low adsorption affinity, while positive holes (h^+) typically oxidize strongly adsorbed compounds. For dissolved organic carbon (DOC) mineralization to CO_2 and H_2O , the process partially depends on the adsorption and subsequent hole-mediated oxidation of final degradation products (including low molecular weight carboxylic acids, ketones, and aldehydes) [6]. When these final products have pK_a values lower than the point of zero charge (PZC) of the catalyst, mineralization efficiency declines at pH values above PZC due to electrostatic repulsion between the negatively charged catalyst surface and the ionized organic compounds.

To directly modify the TiO_2 surface electronic properties and broaden the absorption of light, thus improving the efficiency of the charge separation on the TiO_2 surface, the doping modification of TiO_2 was previously introduced, including non-metallic ions or metal ions, like Co, Ni, Pt [7,8] or incorporation of photoactive TiO_2 into a geo-polymer [9]. Despite their potential as nano- TiO_2 photocatalysts, they face several significant challenges [10,11]:

- Photo-induced electron-positive hole pairs tend to recombine rapidly, reducing catalytic efficiency;
- Poor utilization of the solar spectrum limits practical applications in sunlight;
- Nanoparticles frequently agglomerate, decreasing available reactive surface area;
- Recovery of the nanomaterial from aqueous environments remains technically difficult.

The efficiency of the TiO_2 catalyst supported by modified waste fly ash (FA) was demonstrated [12]. The increased specific surface area of the support material provides additional adsorption sites for TiO_2 , thereby enhancing its photocatalytic efficiency and consequently increasing its potential for pollutant removal.

FA is usually produced by thermal power plants and is a material from the category of micron-sized aluminosilicates with an important content of Si, Al, and minor elements, like Na, K, Ca, Mg [13], and if it is disposed improperly, it can generate environmental issues [14]. A different type of components defines FA, and cenospheres are one of them, characterized by a spherical form with a high content of aluminum and silica. Cenospheres offer significant advantages in composite materials by decreasing density, enhancing thermal insulation properties, strengthening impact resistance, and minimizing shrinkage and warpage issues. Because of other good properties like good porosity and mechanical strength, FA can be successfully used for the preparation of different nanocomposites used in wastewater treatment [15,16].

An innovative approach involving the integration of TiO_2 onto FA cenosphere particles as supporting carriers that enhances photocatalytic efficiency was proposed [17]. The large particle size of FA and oxidic compounds like SiO_2 , Al_2O_3 , MgO and Fe_2O_3 help for TiO_2 immobilization [16].

Several recent studies illustrate the growing interest in FA- TiO_2 composites for water treatment applications. Sharma et al. [18] synthesized TiO_2 and FA- TiO_2 composites (0.5–5 wt% TiO_2) via sol–gel and wet-impregnation methods and evaluated their adsorption

and photocatalytic performance on fuchsin blue dye. The 5 wt% FA-TiO₂ catalyst reached a maximum adsorption capacity of 20.32 mg/g (76% removal) and 88% photocatalytic degradation after 180 min of UV irradiation, remaining effective over five reuse cycles. Similarly, Visa et al. [19] valorized Class F fly ash from a Romanian thermal power plant into a composite with TiO₂ and platinum nanoparticles, synthesized via mild hydrothermal treatment. The platinum doping extended the composite's photocatalytic activity into the visible range (bandgap 2.1 eV) and achieved combined adsorption–photocatalytic removal efficiencies of up to 93.43% for industrial azo dyes when supplemented with H₂O₂. More recently, Xue et al. [20] demonstrated a one-step hydrothermal route converting FA directly into an X-type zeolite-TiO₂ composite, exploiting fly ash's high silicon and aluminum content; this approach achieved 98.36% removal of methylene blue under optimized conditions, underscoring fly ash's potential as a low-cost precursor for high-value catalytic zeolite supports. Collectively, these studies confirm that FA-TiO₂ composites, synthesized through diverse routes including sol–gel, wet-impregnation, and hydrothermal methods, offer an effective and sustainable approach for the simultaneous valorization of FA waste and the removal of organic pollutants from wastewater.

Despite the environmental and health concerns associated with FA, including its potential heavy metal content and classification as a hazardous waste under certain regulatory frameworks, its valorization as a secondary raw material offers a net benefit when properly managed. Uncontrolled disposal of FA in landfills or ash ponds poses ongoing risks of leaching, dust dispersion, and soil/water contamination over time, with no economic return. In contrast, incorporating FA into a stabilized TiO₂-based composite immobilizes the material within a solid matrix, potentially reducing its bioavailability and leaching potential compared to untreated FA, while simultaneously converting a waste stream into a functional material with photocatalytic and adsorptive value. This dual benefit—waste diversion from landfills and the low-cost synthesis of an active water-treatment material—aligns with circular economy principles and offers an economic incentive that pure waste remediation does not.

In this study, composite materials (with various percentages of TiO₂/FA) with adsorption and photocatalytic properties were used in wastewater treatment, taking advantage of TiO₂ as a photocatalyst and FA as a very good adsorbent for the removal of organic pollutants from wastewater. The composites catalytic materials were prepared using FA provided from a Romanian Thermal Plant.

Notably, most prior studies on FA-TiO₂ composites have evaluated performance using model dye solutions (e.g., fuchsin blue, azo dyes, methylene blue) under controlled, single-pollutant conditions. In contrast, the present study assesses photocatalytic performance directly on real municipal wastewater, using COD as the main organic load indicator, offering a more application-relevant evaluation of the composite's treatment potential under complex, multi-pollutant conditions representative of actual discharge streams. The characterization of real municipal wastewater used is presented within Appendix A Table A1.

2. Results and Discussion

2.1. Characterization of Catalysts

2.1.1. Scanning Electron Microscopy

The Scanning Electron Microscopic (SEM) images showed a similar structure of the obtained catalysts with an obvious increase in the amount of TiO₂ on the FA cenospheres. The structural characteristics of the FA-TiO₂ composites were revealed, particularly the effect of the TiO₂ concentration on the coverage of the FA particles (see Figure 1).

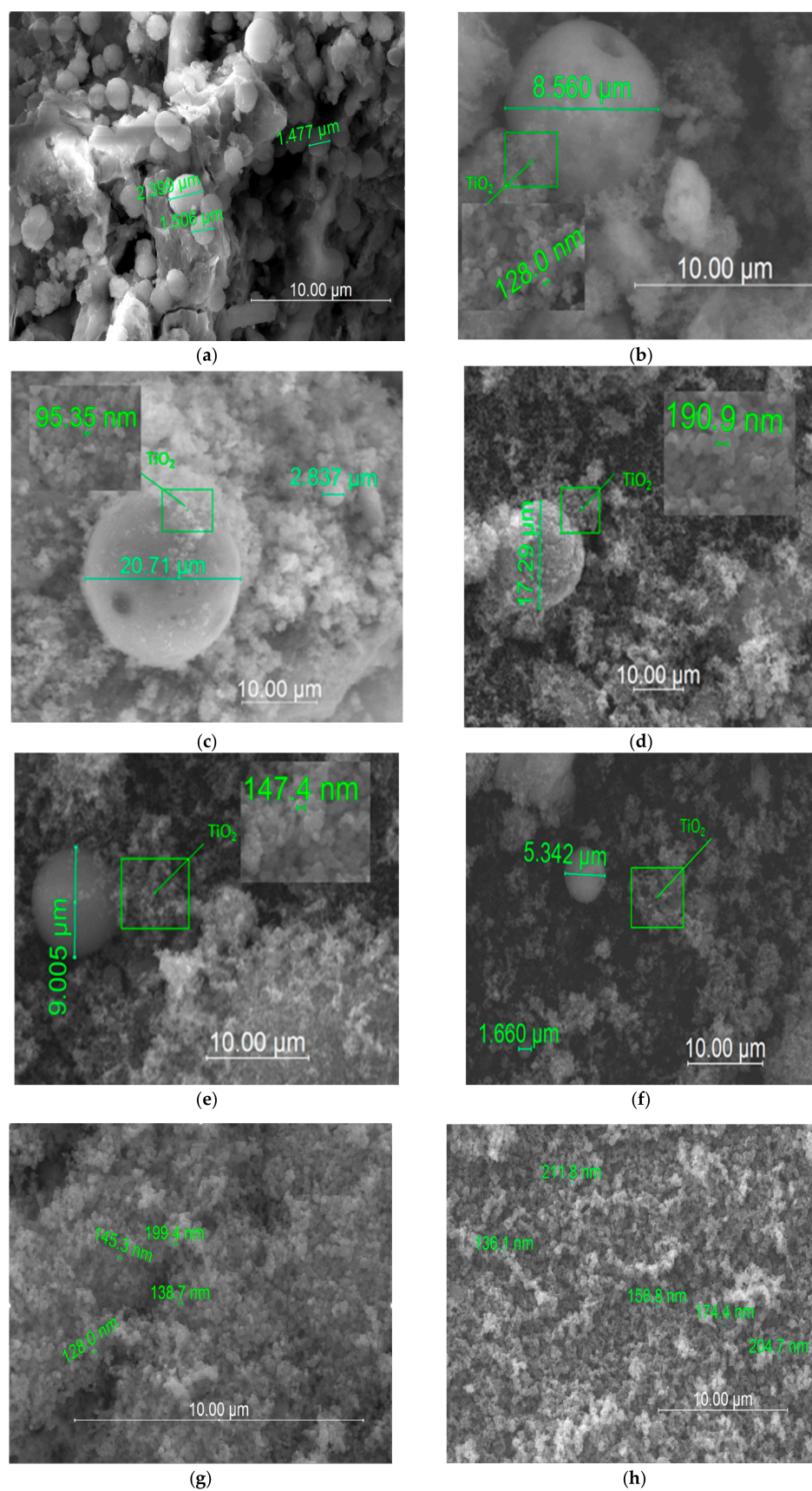


Figure 1. SEM images: (a) 100% FA (Ash); (b) 25% TiO_2 -75%FA (C25); (c) 50% TiO_2 -50%FA (C50); (d) 70% TiO_2 -30%FA (C70); (e) 80% TiO_2 -20%FA (C80); (f) 90% TiO_2 -10%FA (C90); (g) 100% TiO_2 (C100); (h) commercial TiO_2 (TiO_2 p.a.).

Scanning Electron Microscopy (SEM) investigations revealed insights regarding the synthesized catalysts' morphology, which confirmed that TiO_2 had been successfully deposited onto the FA cenosphere supports (Figure 1). Figure 1a shows that raw FA particles retain their natural spherical shape and smooth surface. This characteristic makes them a durable and porous platform for catalyst immobilization. Raising the TiO_2 loading from 25% to 90% (Figure 1b–f) led to a corresponding rise in surface coverage, as nanoparticles clustered together and attached to oxide components (SiO_2 , Al_2O_3 , Fe_2O_3 , and CaO) inherent to the FA. By comparison, pure TiO_2 samples (Figure 1g,h) formed a uniform, highly porous structure on their own. The SEM investigation suggests that the FA substrate helps disperse the TiO_2 nanoparticles more evenly and reduces localized agglomeration. However, this morphological benefit does not translate into improved degradation performance at higher FA content, since it is outweighed by the reduction in the photoactive anatase phase and surface hydroxyl density confirmed by XRD and FTIR analysis (Sections 2.1.3 and 2.1.4).

2.1.2. Wavelength Dispersive X-Ray Fluorescence (WDXRF) Spectroscopy

WDXRF spectroscopy was applied to determine chemical composition of studied samples, as it is detailed in Section 3.2.2. Element concentrations were measured and subsequently reported as oxides using stoichiometric conversion. This approach was considered to better reflect the predominant oxidized forms of elements in studied matrices (fly ashes), and to facilitate comparison with literature data.

The TiO_2 content is presented in Figure 2a. As indicated by the percentages of the XRF measurements, the ash contains primarily silicates and aluminosilicates (Al_2O_3 , SiO_2 , MgO , CaO , K_2O , and Fe_2O_3), and sulphates. The samples obtained by calcination of only $\text{Ti}(\text{iOPr})_4$ have the XRF results closely matching those of a pure TiO_2 reference (Merck). The primary components found— SiO_2 , Al_2O_3 , Fe_2O_3 , K_2O , CaO , MgO and SO_3 —show a gradual decrease, as illustrated in Figure 2b,c.

2.1.3. X-Ray Diffraction (XRD) Analysis

Figure 3 presents the comparative X-ray diffraction patterns of the TiO_2 sample synthesized from titanium isopropoxide— $\text{Ti}(\text{OiPr})_4$ and the TiO_2 –FA materials after calcination. The C100 sample exhibited diffraction peaks at approximately 25.3° (strongest anatase peak), 38.0° , 48.20° , 54.50° , 62.8° , 70° and 75.40° , which are consistent with the characteristic reflections of anatase TiO_2 . The strongest reflection at 25.3° was assigned to the anatase (101) plane. No distinct reflection was observed near 27.4° , corresponding to the principal rutile (110) plane, and the additional characteristic rutile reflections near 36.1° and 41.2° were not identified as a consistent set. Consequently, anatase was considered the predominant crystalline TiO_2 phase, while the presence of a significant rutile fraction was not supported by the XRD results [21].

As the nominal proportion of $\text{Ti}(\text{OiPr})_4$ in the initial formulation increased, the anatase reflections became progressively more prominent. This trend indicates an increasing contribution from precursor-derived crystalline TiO_2 but should not be interpreted as a direct quantitative relationship with the final TiO_2 mass fraction. In the C25 and C50 samples, the anatase reflections were weak because of the lower amount of precursor-derived TiO_2 and the stronger contribution of the fly-ash matrix.

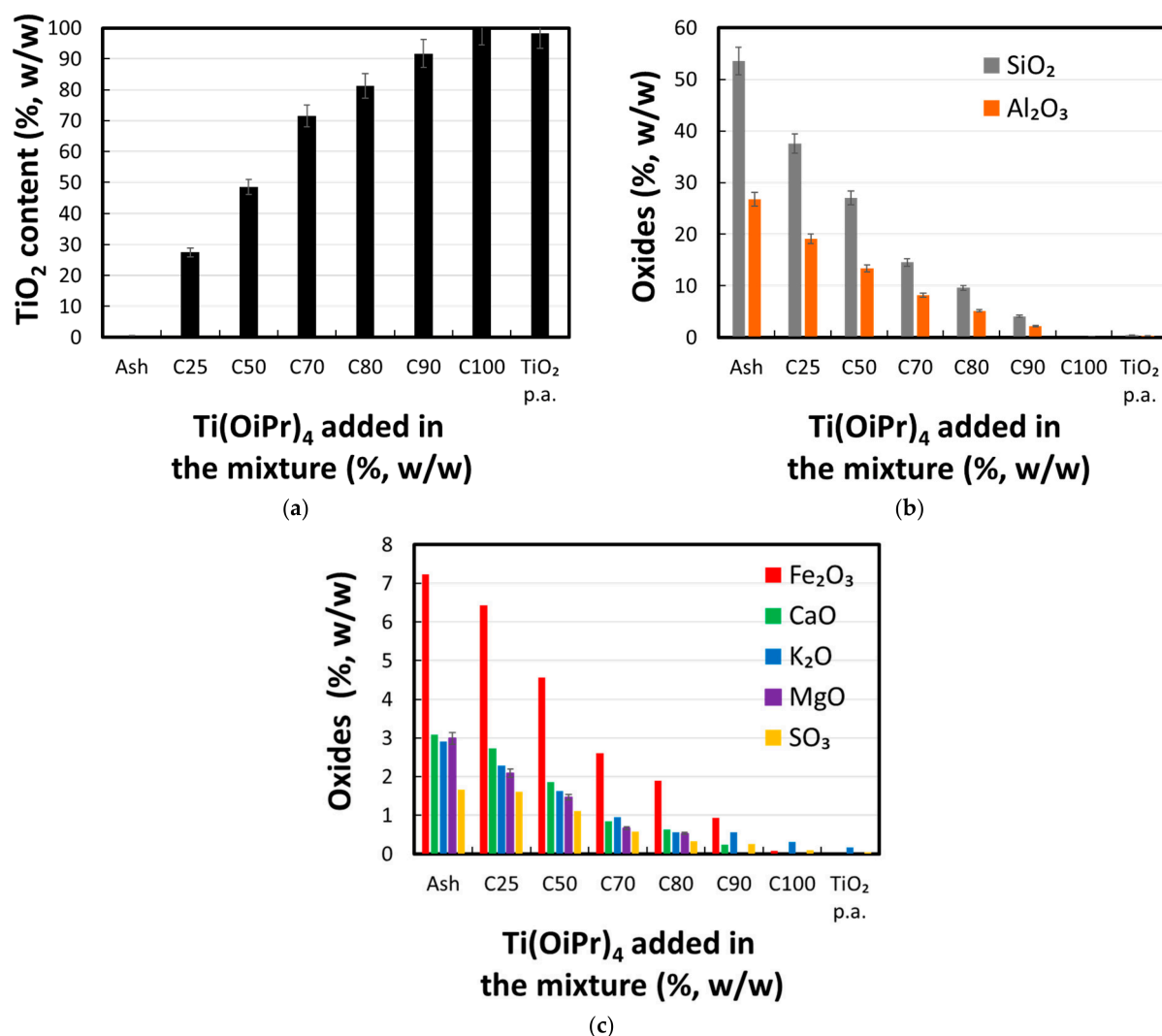


Figure 2. WDXRF results: (a) TiO_2 content; (b) SiO_2 and Al_2O_3 content; (c) SiO_2 , Al_2O_3 , Fe_2O_3 , K_2O , CaO , MgO , SO_3 content.

The XRD results of FA (black line) were considered together with XRF data that show the oxides' composition of SiO_2 53.5%, Al_2O_3 28.60%, Fe_2O_3 6.47%, CaO 2.60%, MgO 3.16%, and K_2O 2.70% as main oxide constituents in the FA. The major peaks present in the ash diffractogram are 26.9° , which is characteristic of quartz's (100) reflection, and additional smaller peaks around 50.2° , 60.1° , and 68° also matched higher order quartz reflections such as (112), (202), (301), consistent with common FA XRD patterns [22]. The FA-related reflection near $26.6\text{--}26.9^\circ$ was assigned to the (101) plane of α -quartz. This peak remained visible as a shoulder adjacent to the anatase reflection at 25.3° , even in samples prepared with relatively high nominal $\text{Ti}(\text{OiPr})_4$ proportions. Additional reflections may be attributed to quartz, mullite, and minor iron-containing crystalline phases. The XRF results, showing high SiO_2 and Al_2O_3 contents, are consistent with a silicoaluminous FA containing quartz, mullite, and an amorphous aluminosilicate fraction.

The progressive broadening and reduced definition of the anatase reflections with increasing FA proportion may arise from the overlap of anatase and ash-related diffraction peaks, dilution of the TiO_2 crystalline phase, crystallite-size effects, microstrain and the contribution of amorphous aluminosilicate material. It was observed that the peak at 25.30° remains unchanged for samples with a TiO_2 content above 70%, whereas in samples with lower TiO_2 content, the TiO_2 anatase peaks are barely visible. Another finding is that the

indication of quartz (26.9° peak) was still visible even for samples with 80% TiO_2 as a shoulder next to the peak of TiO_2 anatase at 25.30° .

Since no systematic displacement of the anatase reflections was observed, the XRD data do not provide conclusive evidence for the formation of a new crystalline titanium–silicate phase. Instead, they indicate that anatase TiO_2 coexists with the crystalline and amorphous constituents of the FA.

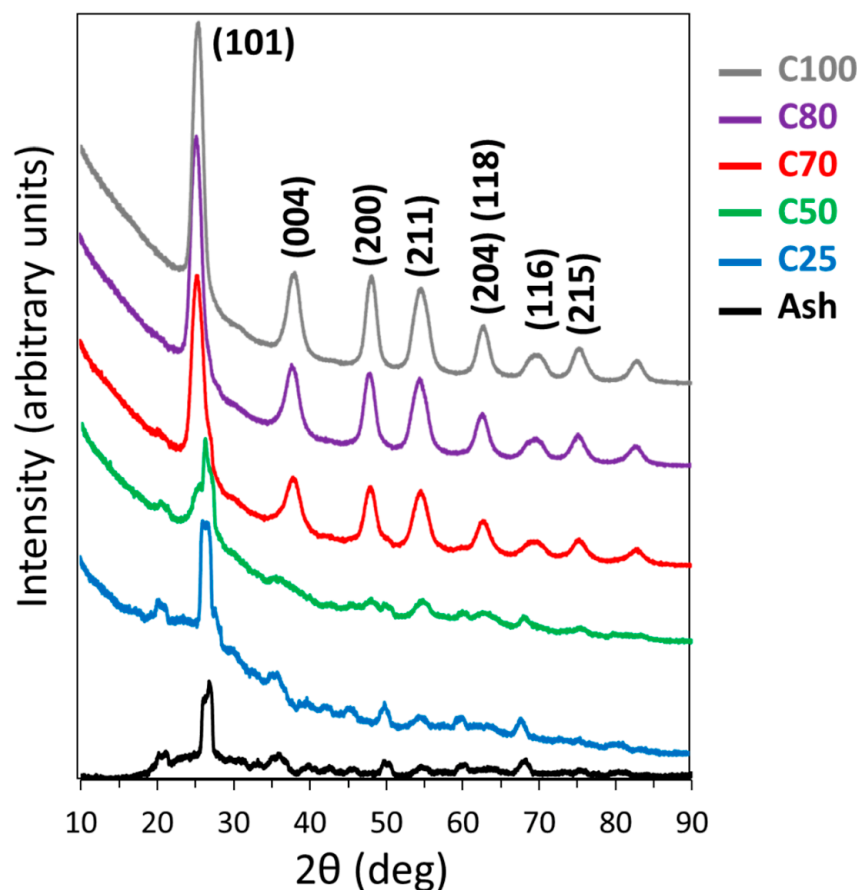


Figure 3. X-ray diffractograms.

2.1.4. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The overall shape of the FTIR spectra, together with the presence of some characteristic absorption bands, provided relevant insights into the structural features of the samples, as it is discussed in detail below. The observed trends were consistent with the results obtained from XRF and XRD analysis that confirmed the presence of silicate and aluminosilicate structures, typical for materials derived from natural minerals or combustion residues.

The first observation, as shown by Figure 4, was that the O–H vibration band is intense and broad in the samples containing TiO_2 , while it is weak in the ash samples (Figure 4a). The broad OH band at 3300 cm^{-1} is typically associated with hydroxyl groups or adsorbed water. The increase in intensity for samples with TiO_2 suggests that titanium oxides promote the formation or retention of surface hydroxyl groups. This could be due to the hydrophilic nature of TiO_2 , which readily adsorbs water or forms hydroxyl groups on its surface. The weak OH band in FA samples indicated a lower capacity for water adsorption or fewer hydroxyl groups.

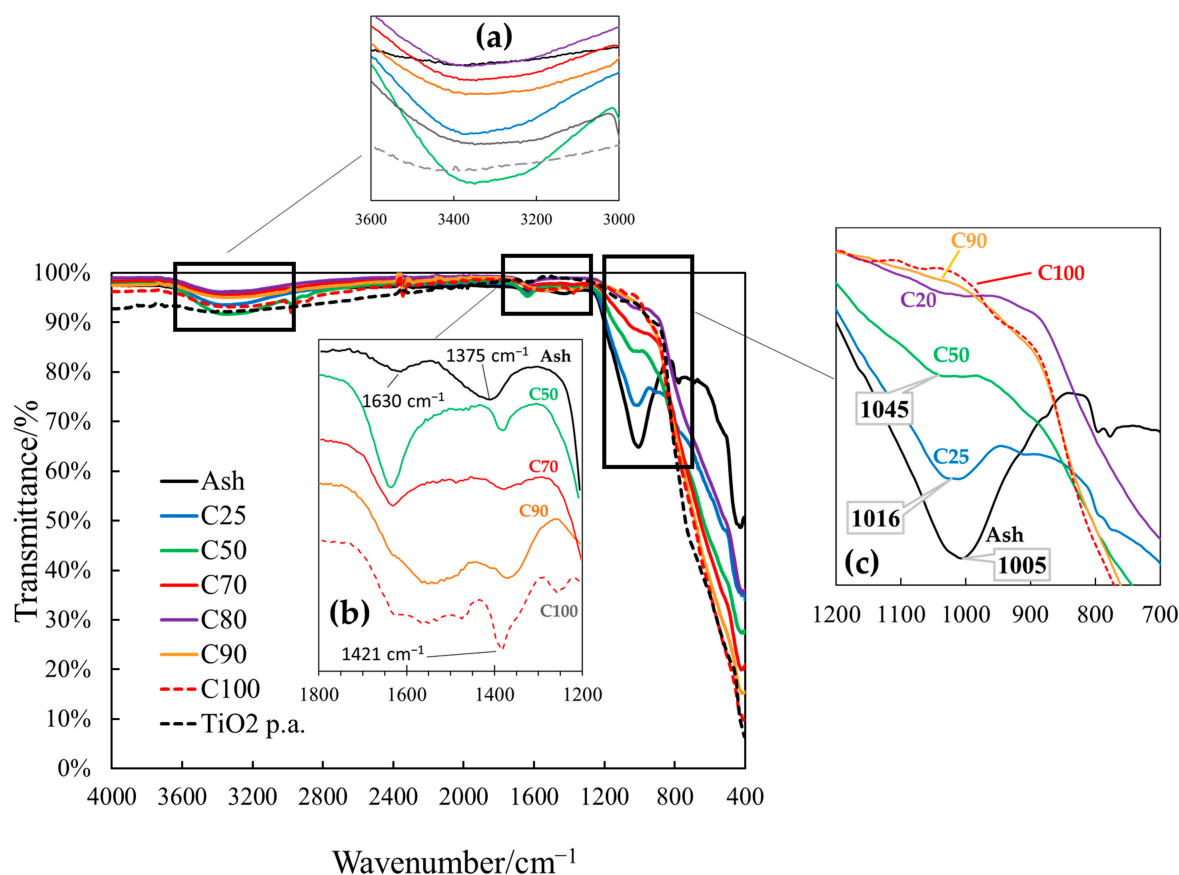


Figure 4. FTIR spectra of tested samples with various ash contents. Insets (a) 3000–3600 cm^{-1} ; (b) 1200–1800 cm^{-1} ; (c) 700–1200 cm^{-1} domains.

Another important feature in the IR spectra was the band at 1003 cm^{-1} . It was observed that the ash samples showed a strong band at 1003 cm^{-1} . In samples obtained by mixing 25–75% $\text{Ti}(\text{iOPr})_4$, the band shifts to 1045 cm^{-1} and becomes a shoulder. For the synthesized TiO_2 (C100 sample), the band was absent. The 1003 cm^{-1} band is characteristic of Si–O–Si stretching vibrations in silicates or aluminosilicates. The decrease in intensity and eventual disappearance of this band as the percentage of $\text{Ti}(\text{OiPr})_4$ added to the ash increases indicated that the silicate structure is being disrupted or modified by the incorporation of titanium. This finding correlated well with the XRF data presented in Figure 2.

The shift in the ash-related band from 1005 cm^{-1} to approximately 1045 cm^{-1} suggested the formation of a titanium–silicate phase or Ti–O–Si linkages, which alter the vibrational characteristics of the Si–O–Si network, as shown in Figure 4c. In the synthesized TiO_2 and blank samples, the absence of the 1005 cm^{-1} band confirmed that no detectable silicate species were present, with titanium oxide phases being predominant in these materials.

The FTIR spectra confirmed the presence of the strongly absorbing Ti–O and Ti–O–Ti lattice-vibration region below approximately 900 cm^{-1} . In the spectra of both the commercial and synthesized TiO_2 samples, this region appeared as a steep and largely unresolved decrease in transmittance rather than as a series of well-separated bands. Such broad low-wavenumber absorption is characteristic of the Ti–O framework and is reported for TiO_2 polymorphs, including anatase. In the present samples, identification of the crystalline TiO_2 phase was based on XRD and supported by Raman spectroscopy, which indicate anatase as the predominant crystalline phase [23,24].

An important characteristic of the IR spectra was that no absorption bands were observed in the C-H region, indicating that all organic material has been eliminated during the burning process. This confirmed complete combustion of the organic components in $\text{Ti}(\text{iOPr})_4$, leaving only inorganic residues.

Furthermore, it was observed that a strong absorption band at 400 cm^{-1} , which is related to the Ti-O-Ti vibration, replaces medium peaks at 690 , 775 , and 796 cm^{-1} , which correspond to the Si-O bending vibrations. The small peak at 1435 cm^{-1} completely disappeared for samples with titanium, while samples with titanium presented two small peaks at 1546 and 1358 cm^{-1} , the intensity being increased when the titanium content increases (Figure 4b), indicating the formation of the new Ti-O bonds [25].

2.1.5. RAMAN Analysis

Figure 5 shows two regions that underwent significant modifications with the modification of ash content in the mixture.

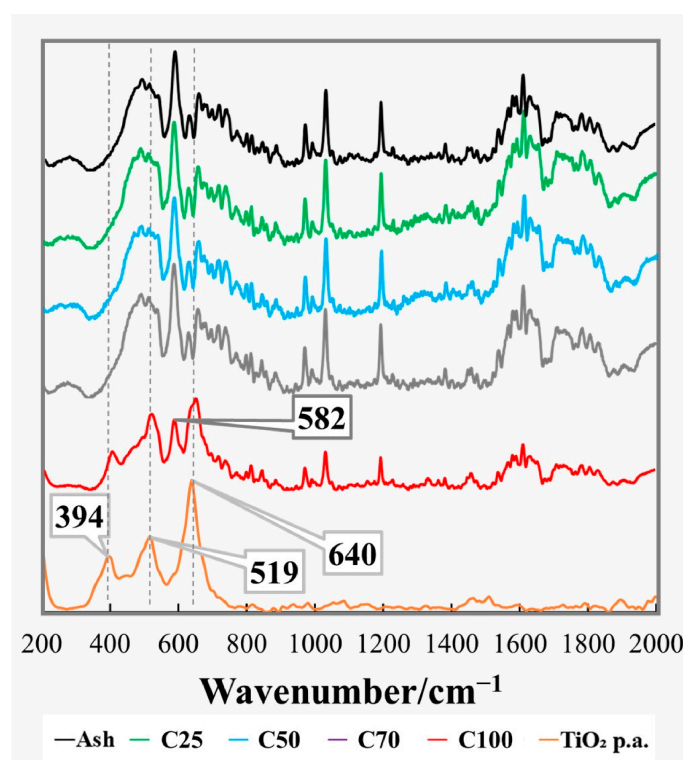


Figure 5. Raman spectra of tested samples with different ash content.

The commercial TiO_2 sample exhibited Raman bands characteristic of the anatase phase, including the modes located near 399 , 513 – 519 , and 639 cm^{-1} . In contrast, the TiO_2 synthesized from $\text{Ti}(\text{OiPr})_4$ and the TiO_2 -FA composites showed substantially different spectral profiles, particularly within the 400 – 600 cm^{-1} region. A band centered at approximately 582 cm^{-1} was observed for the synthesized TiO_2 sample, C100, and became more pronounced in the FA-containing composites. This band cannot be assigned exclusively to rutile, whose principal A_{1g} mode is normally located near 612 cm^{-1} . Its position is also consistent with the brookite B_{2g} mode reported near 581 – 585 cm^{-1} . Therefore, the C100 spectrum suggests that the TiO_2 obtained from $\text{Ti}(\text{OiPr})_4$ may contain brookite or a mixed and structurally disordered TiO_2 phase rather than phase-pure anatase [26].

In the composite samples, the feature near 582 cm^{-1} is likely intensified by overlapping contributions from the TiO_2 phases and the FA matrix. Mullite, an important crystalline aluminosilicate constituent of FA, exhibits Raman bands around 595 – 600 cm^{-1} , while

quartz contributes strongly near 464 cm^{-1} . A possible contribution from the broad rutile mode near 612 cm^{-1} was excluded. The absence of the characteristic rutile reflection in XRD analysis at 27.4° is consistent with the absence of clear rutile Raman modes near 447 and 612 cm^{-1} . Consequently, the band near 582 cm^{-1} is interpreted as a composite spectral feature rather than as an unambiguous marker of a single TiO_2 polymorph.

Additional FA-related features near approximately 938 and 1126 cm^{-1} may be associated with mullite and other aluminosilicate structures, whereas the broad character of this region may also reflect the amorphous aluminosilicate glass fraction [26].

The additional Raman feature centered at approximately 582 cm^{-1} , which is not characteristic of phase-pure anatase, is compatible with a minor brookite-related or structurally disordered TiO_2 contribution. However, because this feature alone is insufficient for an unambiguous phase assignment and the XRD results identify anatase as the predominant crystalline phase, the possible presence of brookite is considered tentative. The possible coexistence of anatase and a minor brookite fraction may be relevant to photocatalytic degradation, since anatase–brookite phase junctions have been reported to promote charge-carrier separation and reduce effective electron–hole recombination [27]. Brookite itself can also exhibit favorable charge-trapping characteristics for photocatalytic oxidation and reduction. However, because neither the brookite fraction nor charge-carrier lifetimes were directly determined in the present study, such an effect cannot be established conclusively and is considered only as a possible contribution to the observed photocatalytic behavior.

2.1.6. Point of Zero Charge

Solid metal oxides in contact with aqueous solutions typically become hydrated and form a monolayer of surface hydroxyl groups that may become protonated or deprotonated, depending on the $\text{H}^+(\text{aq.})$ concentration. This amphoteric behavior allows the oxide particles to develop electrical charges that are either positive (when they receive protons) or negative (when they release protons). The point of zero charge of a metal oxide mixture corresponds to the pH where the net surface charge of the heterogeneous mixture is zero [28,29]:

The surface charge of the investigated materials results from the protonation and deprotonation of hydroxylated sites exposed at the solid–water interface. Figure 6 schematically illustrates the acid–base equilibria of Ti-OH groups, which become positively charged through protonation at pH values below the point of zero charge and negatively charged through deprotonation at higher pH values. However, for the FA- TiO_2 composites, the measured pH_{pzc} represents the combined response of TiO_2 and the different mineral phases present in the ash rather than the behavior of TiO_2 alone.

The FA contained predominantly SiO_2 and Al_2O_3 , together with Fe_2O_3 and smaller amounts of Ca-, Mg-, and alkali-containing phases as indicated by the XRF results. Hydration of these phases generates chemically different surface sites, including silanol groups, $-\text{Si-OH}$, aluminol groups, $-\text{Al-OH}$, and hydroxyl groups associated with iron-containing phases. These sites undergo acid–base equilibria analogous to those of Ti-OH groups, generating species with different acidities.

In addition, partial dissolution or ion exchange involving calcium, magnesium, and alkali-containing phases may influence the pH of the suspension during the measurement. Considering these competitive processes that occur at the interface, we can presume that the measured pH_{pzc} would not be evolving linearly with the added $\text{Ti}(\text{OPr})_4$ content. Furthermore, the value of pH_{pzc} depends not only on the mass fractions of the components but also on their specific surface areas, surface coverage, accessibility, and spatial distribution.

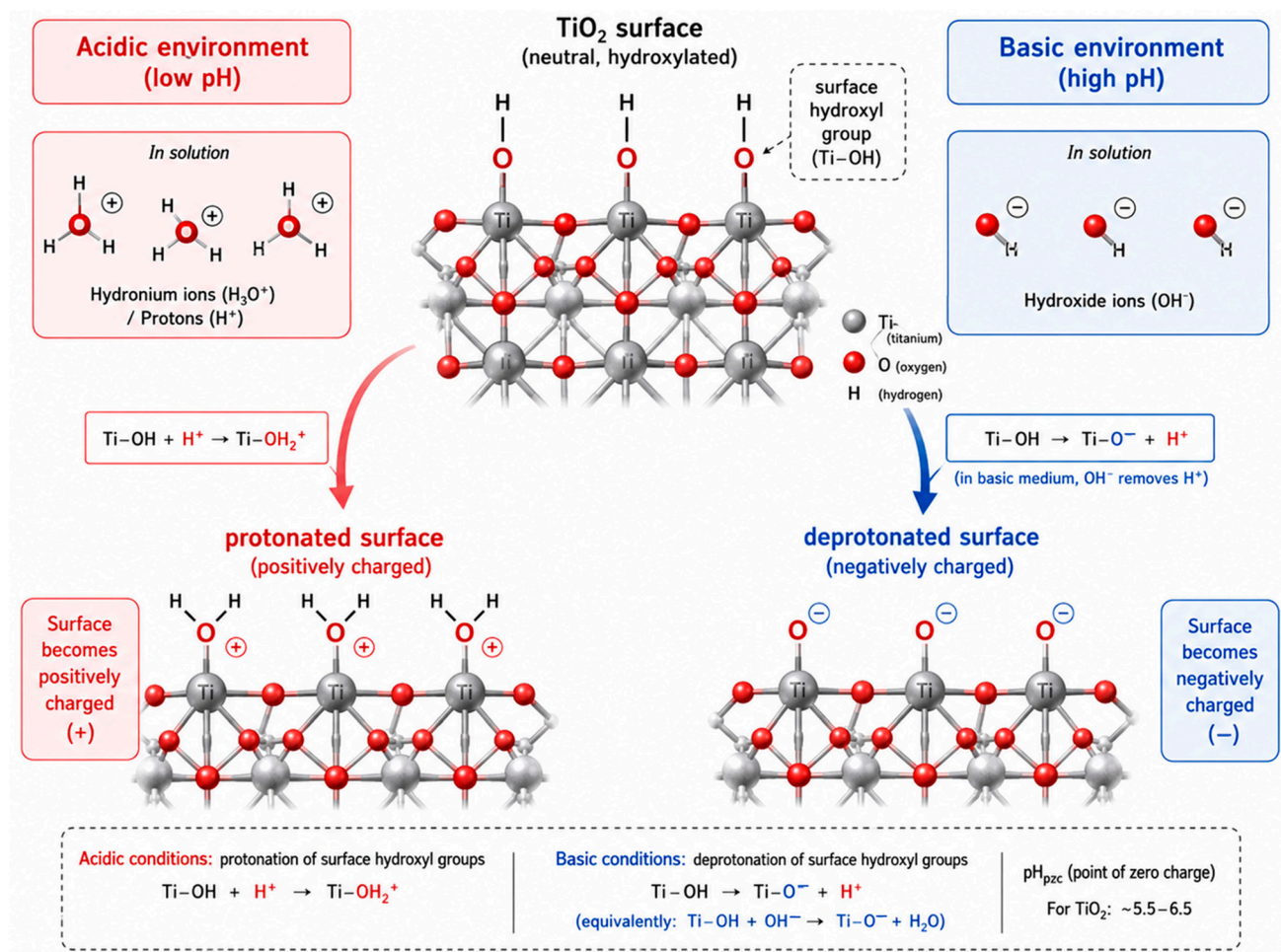


Figure 6. Simplified representation of the protonation and deprotonation equilibria of hydroxyl groups on a TiO_2 surface.

The $\text{pK}_{\text{a}1}$ and $\text{pK}_{\text{a}2}$ values were extracted from the potentiometric titration curves. The pH values were plotted against cumulative acid volume, and the first derivative (dpH/dV) of this curve was calculated. The two inflection points of the titration curve appear as two distinct drops in the first-derivative plot, and the pH values at these drops were taken as $\text{pK}_{\text{a}1}$ and $\text{pK}_{\text{a}2}$, corresponding to the two sequential protonation/deprotonation equilibria of the amphoteric surface hydroxyl groups [29]. The point of zero charge (pH_{pzc}) was subsequently calculated as the average of $\text{pK}_{\text{a}1}$ and $\text{pK}_{\text{a}2}$ (see Equation (1)).

Figure 7 presents the pH values and their derivatives as a function of cumulative acid volume. pH corresponding to the point of zero charge was calculated based on the following equation:

$$\text{pH}_{\text{pzc}} = \frac{\text{pK}_{\text{a}1} + \text{pK}_{\text{a}2}}{2} \quad (1)$$

Figure 7 shows that the synthesized TiO_2 sample exhibited a pH_{pzc} of 6.10, whereas the composite samples presented slightly lower values, ranging from 5.76 to 5.95. This relatively narrow interval suggests that TiO_2 -related surface hydroxyl groups remain an important contribution to the interfacial behavior of the composites, while the silicate and aluminosilicate components of the ash cause a modest shift toward more acidic values.

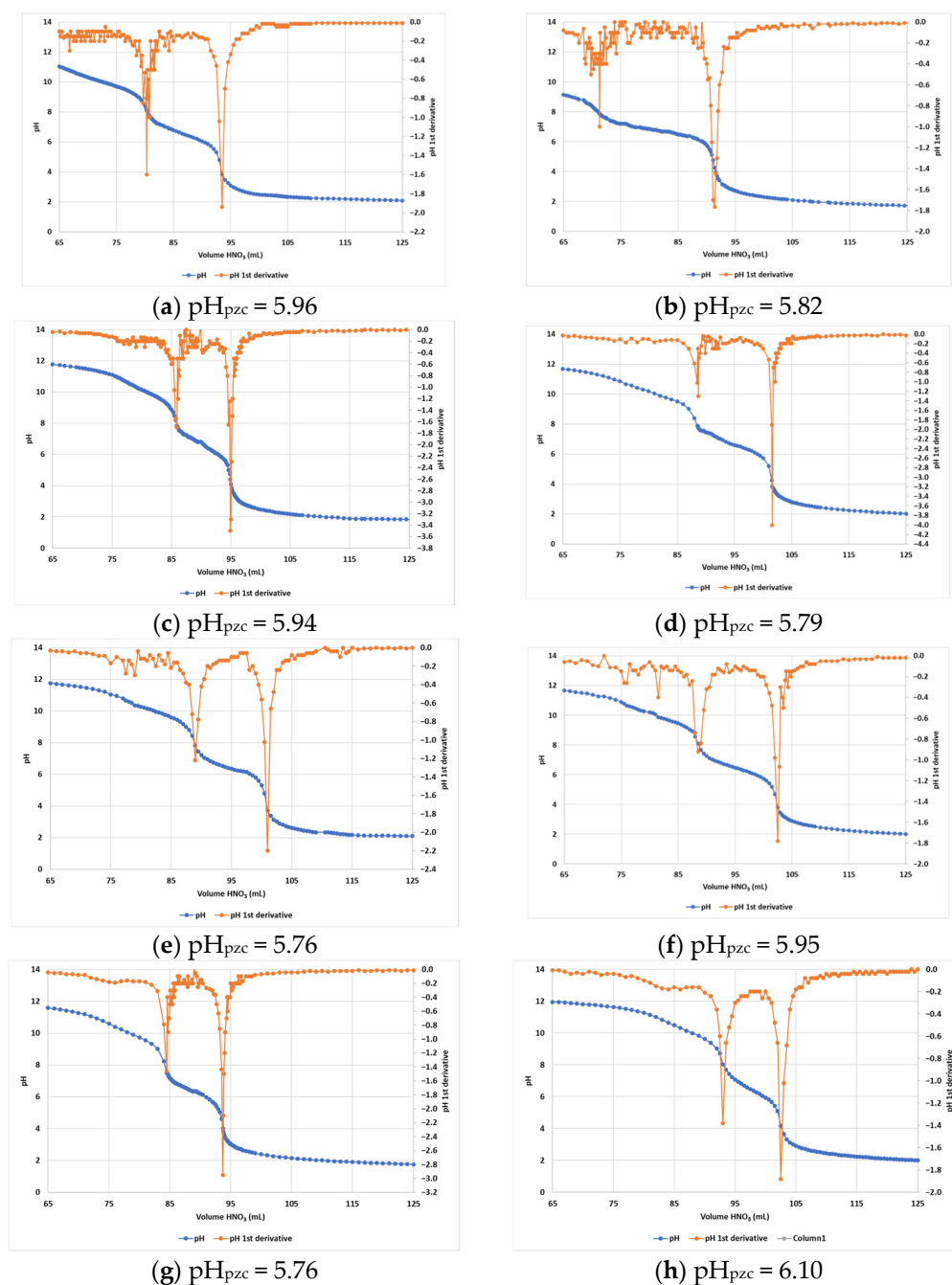


Figure 7. pH variation in the photocatalytic suspension: (a) 100% FA (Ash); (b) 25% TiO_2 –75%FA (C25); (c) 50% TiO_2 –50%FA (C50); (d) 70% TiO_2 –30%FA (C70); (e) 80% TiO_2 –20%FA (C80); (f) 90% TiO_2 –10%FA (C90); (g) 100% TiO_2 (C100); (h) commercial TiO_2 (TiO_2 p.a.).

Nevertheless, the absence of a monotonic relationship between pH_{pzc} and the nominal $\text{Ti}(\text{O}i\text{Pr})_4$ loading indicates that the point of zero charge is governed by the composition of the accessible surface rather than directly by the bulk precursor proportion. For heterogeneous oxide mixtures, the measured pH_{pzc} depends on the specific surface area, surface distribution, and exposure of the individual phases, and is therefore not expected to follow a simple linear mixing relationship.

2.1.7. Leaching Test on FA

FA leaching test for relevant heavy metals (such as Cr, Pb, Cd, Ni, As) was performed and the results were processed by ICP-EOS (see Table 1).

Table 1. Leaching test of FA.

Metal	Value (mg/L)	Maximum Admissible Value According to Romanian Discharge Limits Norm (mg/L)
As (As ³⁺)	<	0.1
Cd (Cd ²⁺)	0.0002	0.2
Total Cr	<	1.0
Cu (Cu ²⁺)	0.0048	0.1
Mo (Mo ²⁺)	0.0091	0.1
Ni (Ni ²⁺)	0.0063	0.5
Pb (Pb ²⁺)	<	0.2
Se (Se ²⁺)	<	0.1
Zn (Zn ²⁺)	0.0050	0.5

"<" under limit of quantitation (LOQ).

Metal concentrations were compared against the discharge limits established under the Romanian norm for wastewater discharge into natural receivers, and experimental data confirmed that metal concentrations remain within safe discharge limits.

2.2. Photocatalytic Experiments

2.2.1. Influence of TiO₂ Content

Photocatalytic experiments were performed at a constant catalyst dose of 200 mg/L and a total irradiation time of 300 min. The obtained experimental results are presented in Table 2.

Table 2. Influence of TiO₂ content.

Catalyst Sample	TiO ₂ Content (%)	Overall COD Removal Efficiency (%)
No catalyst	-	16.67
C25	25	29.41
C50	50	35.48
C70	70	41.94
C80	80	48.39
C90	90	60.00
C100	100	64.47
Commercial TiO ₂	100	65.38

The monotonic increase in COD removal efficiency with increasing TiO₂ content (Table 2), from 29.41% at 25% TiO₂ to 64.47–65.38% for pure TiO₂, is consistent with the characterization results presented in Section 2.1. Two factors converge to explain the superior performance of the TiO₂-rich composites, particularly C90 (90% TiO₂–10% FA). First, XRD analysis (Section 2.1.3) showed that anatase reflections, corresponding to the photoactive TiO₂ crystalline phase primarily responsible for photocatalytic activity [21], become progressively weaker and less defined with decreasing TiO₂ content, indicating a lower density of active photocatalytic sites in the FA-rich composites. Second, FTIR spectra (Section 2.1.4) showed increasing surface hydroxyl group density with increasing TiO₂ content, consistent with a greater capacity for photogenerated hydroxyl radical formation, the primary oxidative species responsible for organic pollutant degradation in TiO₂-based systems [3]. The C90 composite in particular appears to represent a favorable balance. It retains a sufficiently high fraction of crystalline anatase and surface hydroxyl density to sustain strong photocatalytic activity, while the small FA fraction (10%) still contributes

to nanoparticle dispersion, as observed by SEM (Section 2.1.1), without proportionally diluting the active phase to the extent seen in the lower-TiO₂ composites (C25–C70).

This is consistent with previous reports on FA-TiO₂ composites, where an optimal FA:TiO₂ ratio balancing dispersion/support effects against active-phase dilution has similarly been identified [12,18]. Beyond this optimal range, however, our results show that further increasing TiO₂ content to 100% yields only a marginal additional gain (60.00% for C90 vs. 64.47–65.38% for C100/commercial TiO₂).

2.2.2. Influence of TiO₂ Dose

The influence of catalyst dose was investigated using three TiO₂ doses of 200, 400 and 600 mg/L. In all photocatalytic experiments, prior to irradiation, FA-TiO₂ catalysts were added to municipal wastewater and the suspensions were bubbled with air (50 L/h), in the dark, for 30 min in order to achieve adsorption equilibrium and to avoid the electrons–positive holes recombination.

Average COD removal efficiency (due to adsorption of pollutants on FA-TiO₂ particles) during this period was $7.22\% \pm 4.77\%$. The profiles of [COD]/[COD]₀ vs. time for all experiments are presented within Appendix A, Figure A1.

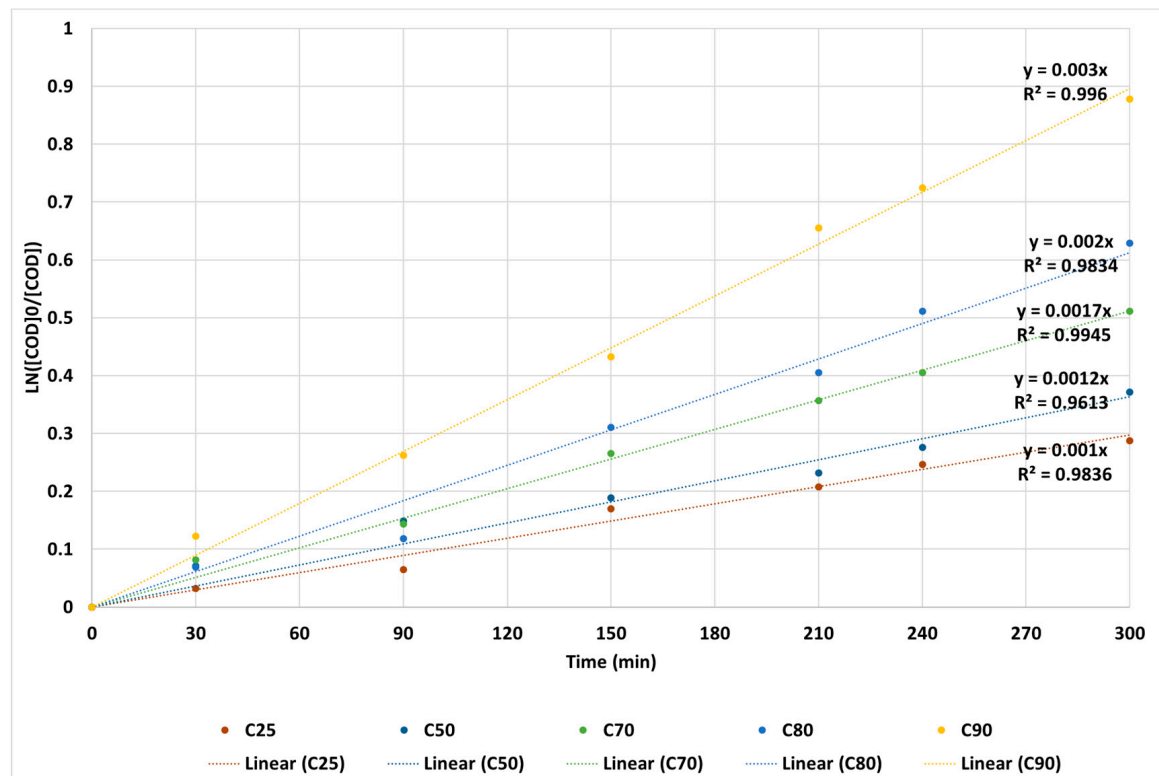
COD values at the moment of irradiation start were used as baselines for the calculation of the apparent pseudo-first order rate constant.

The obtained experimental results are presented in Table 3.

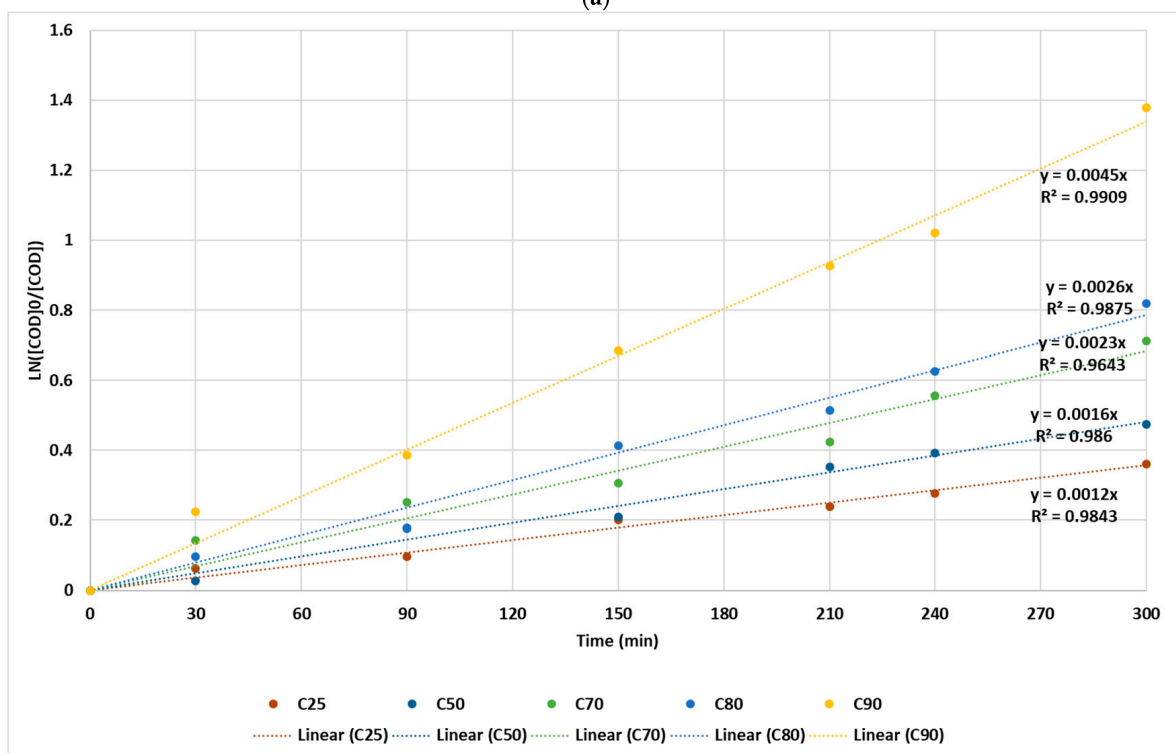
Table 3. Influence of catalyst dose upon COD removal.

Catalyst Sample	Catalyst Dose (mg/L)	Overall COD Removal Efficiency (%)	Apparent Pseudo-First Order Rate Constant (s ^{−1})
C25	200	29.41	1.67×10^{-5}
	400	32.15	2.00×10^{-5}
	600	24.71	1.50×10^{-5}
C50	200	35.48	2.00×10^{-5}
	400	39.47	2.67×10^{-5}
	600	31.43	1.83×10^{-5}
C70	200	41.94	2.83×10^{-5}
	400	56.79	3.83×10^{-5}
	600	39.98	2.50×10^{-5}
C80	200	48.39	3.33×10^{-5}
	400	58.00	4.33×10^{-5}
	600	42.81	2.83×10^{-5}
C90	200	60.00	5.00×10^{-5}
	400	76.67	7.50×10^{-5}
	600	54.99	1.50×10^{-5}

Figure 8 presents the pseudo-first order kinetic of COD removal at 200, 400 and 600 mg/L catalyst doses.



(a)



(b)

Figure 8. Cont.

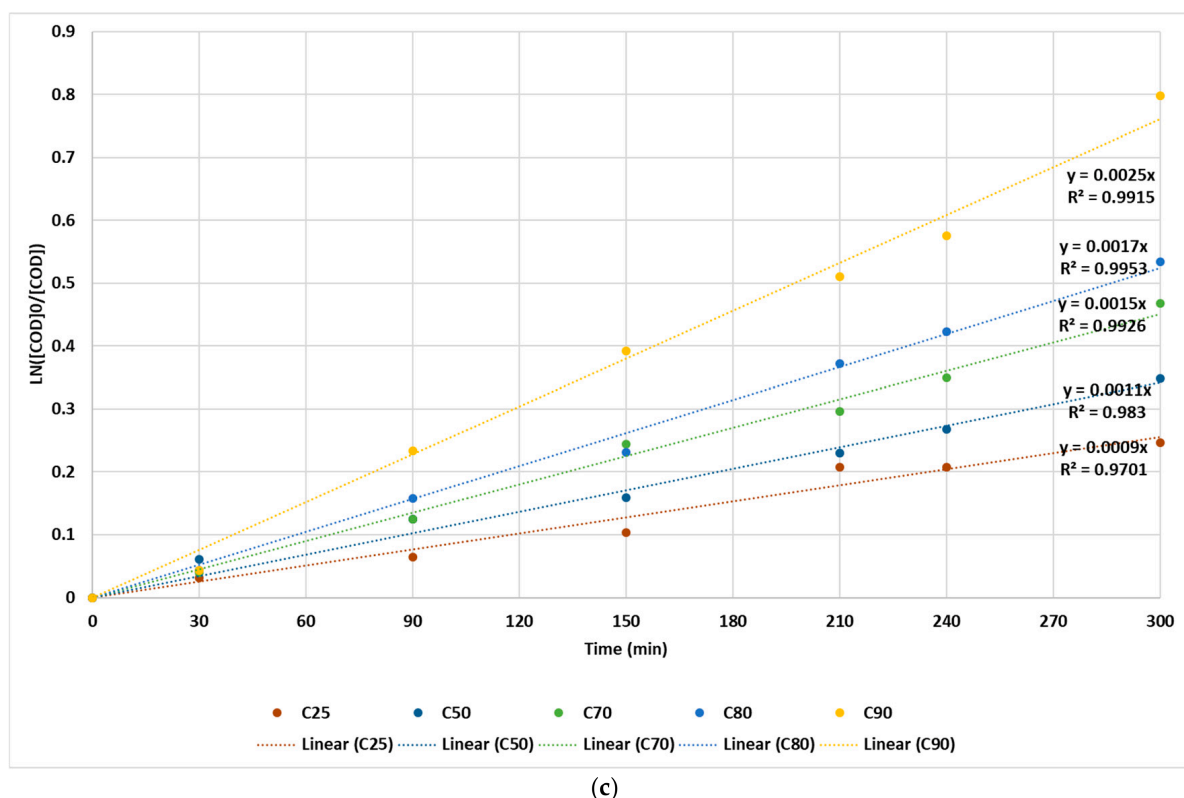


Figure 8. Pseudo-first order kinetic of COD removal. Catalyst doses: (a) 200 mg/L; (b) 400 mg/L; (c) 600 mg/L.

2.3. Comparison with Other Studies

Studies from the last years proved that FA composites have good potential for degradation of organic compounds, but the majority of the studies were focused on the degradation of model compounds like dyes [2,11,12,18]. On the other hand, within the literature, studies can be found focusing on the removal of organic compounds like clofibric acid and carbamazepine under UV-VIS irradiation [30,31]. There are limited studies focused on the degradation of organic compounds from real wastewater [32].

A comparison of the results of this study with similar ones from the literature is presented within Table 4.

Table 4. Comparison with other studies.

Process/Initial Concentration	Results	Conditions	References
Cu/TiO ₂ /FA composite under visible light irradiation 5–25 mg/L methyl orange	99.1%	2 g/L Cu/TiO ₂ /FA	[2]
Nano TiO ₂ on FA cenospheres (FACs) under UV light 10 mg/L methyl orange	95.5%	0.5 g/L FACs-TiO ₂	[11]
FA/TiO ₂ nanocomposite under UV-A irradiation 30 mg/L RR45 dye	95%	1 mg/L FA/TiO ₂	[12]
FA/TiO ₂ under UV light 5–30 mg/L fuchsine dye	$k = 0.0016 \text{ min}^{-1}$ 88%	5 wt% FA-TiO ₂	[18]
UV-VIS with suspended TiO ₂ 20 mg/L clofibric acid	$k = 0.00326 \text{ min}^{-1}$	0.5 g/L TiO ₂	[30]

Table 4. Cont.

Process/Initial Concentration	Results	Conditions	References
Photocatalytic ZnO foams 10 mg/L carbamazepine	$k = 0.0033 \text{ min}^{-1}$	0.5 g/L ZnO	[31]
Fe-TiO ₂ (supported)/Fe-TiO ₂ (supported) + H ₂ O ₂ , 13W LED/natural sunlight, real wastewater, initial TOC = 21.5 mg/L	Final TOC in the domain 14.3 ± 1.2 to $17.4 \pm 0.5 \text{ mg/L}$	Solid/liquid ratio of 0.25 g/mL	[32]
UV-VIS with suspended FA-TiO ₂ Initial COD = 244.4–334.4 mgO ₂ /L	$k = 0.0045 \text{ min}^{-1}$ 76.67%	0.4 g/L 90%TiO ₂ -10%FA	This study
	$k = 0.0026 \text{ min}^{-1}$ 58.00%	0.4 g/L 80%TiO ₂ -20%FA	
	$k = 0.0023 \text{ min}^{-1}$ 56.79%	0.4 g/L 70%TiO ₂ -30%FA	
	$k = 0.0016 \text{ min}^{-1}$ 39.47%	0.4 g/L 50%TiO ₂ -50%FA	
	$k = 0.0012 \text{ min}^{-1}$ 32.15%	0.4 g/L 25%TiO ₂ -75%FA	

The results presented in this study show good performance of the process, taking into consideration that degradation tests were performed using real wastewater.

Data indicate that TiO₂ content is indeed the dominant factor governing photocatalytic performance, but for identifiable structural reasons rather than as a standalone empirical correlation. XRD analysis (Section 2.1.3) shows that the anatase reflections—the photoactive crystalline phase—become progressively weaker and less defined as FA content increases, being barely detectable in the lowest-TiO₂ composites (C25, C50). This indicates that increasing TiO₂ loading increases not only total catalyst mass but also, specifically, the amount of photoactive anatase phase available for radical generation. This is corroborated by FTIR results (Section 2.1.4), where the intensity of the O–H stretching band, associated with surface hydroxyl groups that are precursors to photogenerated hydroxyl radicals, increases with TiO₂ content.

However, the results indicate that FA is not merely a diluent. SEM imaging (Section 2.1.1) shows that FA cenospheres promote more even dispersion of TiO₂ nanoparticles and reduce agglomeration relative to pure TiO₂, which by itself would tend to favor exposed surface area in the composites. Despite this structural benefit, the anatase-phase and hydroxyl-density effects dominate, which explains why COD removal still increases monotonically with TiO₂ content up to 100%.

The surface charge (pH_{pzc}) could also explain the trend, since electrostatic interactions between catalyst and pollutants affect adsorption and reactivity. However, pH_{pzc} values for the composites (5.76–5.95) did not varied monotonically with TiO₂ content and remained in a narrow range distinct from that of pure TiO₂ (6.10), indicating that surface charge is governed by the specific surface area and phase distribution of the heterogeneous mixture rather than by the bulk TiO₂:FA ratio. This rules out surface charge as the driver of the observed degradation trend. Similarly, the contribution of dark adsorption to overall COD removal was low and comparable across all samples ($7.22\% \pm 4.77\%$), indicating that differences in photocatalytic (not adsorptive) activity are responsible for the performance ranking.

The identification of anatase as the predominant crystalline TiO₂ phase has important implications for the expected photocatalytic behavior of the investigated materials. Photogenerated electron–hole recombination is one of the principal processes limiting TiO₂

photocatalytic efficiency; however, its kinetics depend strongly on the TiO₂ polymorph. Direct spectroscopic investigations have shown faster charge-carrier recombination in rutile than in anatase, while anatase is generally associated with longer-lived photogenerated carriers and higher photocatalytic activity for many oxidation reactions [33]. Consequently, the predominance of anatase observed in the present samples is favorable for maintaining photocatalytically active charge carriers.

Mixed anatase–rutile TiO₂ systems may exhibit an additional enhancement arising from interfacial charge transfer between the two polymorphs, which can decrease effective electron–hole recombination [34]. In the present study, however, the characteristic XRD reflections of rutile were not detected as a consistent set, indicating that any rutile contribution is minor. Therefore, an anatase–rutile heterojunction mechanism is unlikely to represent the principal origin of the photocatalytic behavior of the investigated TiO₂–FA composites. Instead, the fly-ash matrix may influence the photocatalytic response through several interfacial and surface effects. The silica- and alumina-rich phases can act as a support for TiO₂, affecting particle dispersion, accessible surface area, and pollutant adsorption, whereas iron-containing phases may additionally participate in interfacial charge-transfer processes. Therefore, the photocatalytic properties of the present composites should be considered as resulting from the combined effects of the predominantly anatase TiO₂ phase and the heterogeneous TiO₂–FA interface rather than from an anatase–rutile synergistic effect. Nevertheless, because charge-carrier lifetimes were not measured directly in the present study, the influence of the fly ash on electron–hole recombination should be regarded as a plausible mechanism rather than as experimentally demonstrated.

These results are consistent with other recent studies applying TiO₂-based photocatalysts to real wastewater matrices. Rosa and Di Palma [32] demonstrated a solar-driven continuous-flow system using Fe-doped TiO₂ immobilized on polystyrene, achieving up to 99.8% rhodamine B removal and a TOC reduction from 21.5 to 14.3 mg/L (approximately 33% mineralization) in real pharmaceutical wastewater under natural solar irradiation with H₂O₂ enhancement. While their system targeted a single model dye spiked into real wastewater under continuous-flow conditions, our study evaluates the intrinsic organic load (COD) of real municipal wastewater directly, without pollutant spiking, under batch UV irradiation. The comparable order of magnitude in mineralization efficiency between the two studies supports the feasibility of TiO₂-based composites, including low-cost fly-ash-supported variants such as ours, for real wastewater applications, while also highlighting continuous-flow, solar-driven operation as a promising direction for future scale-up of our system. Therefore, the use of FA-TiO₂ seems to offer good perspectives for the development of low-cost wastewater treatment processes.

3. Materials and Methods

3.1. Materials

3.1.1. Synthesis of TiO₂

Titanium dioxide was prepared via sol–gel method using Titanium (IV) isopropoxide (Sigma Aldrich Chemie GmbH, Steinheim, Germany) that was added gradually to ethanol solution under continuous stirring (500 rpm) at room temperature for two hours, and then, a mixture of ultrapure water and ethanol (Chimreactiv, Bucharest, Romania) was added dropwise (in small portions under vigorous stirring) to perform the hydrolysis step. Resulted solutions were maintained under vigorous stirring for 3 h at room temperature. Polycondensation and chain growth followed by gelling were obtained after 72 h, dried at 80 °C for 2 h and calcinated at 400 °C for the next 2 h to obtain crystalline TiO₂ nanoparticles prior to characterization.

3.1.2. Synthesis of FA-TiO₂

FA was provided by a Romanian Thermal Plant. At the beginning, FA was washed with ultrapure water for 1 h until the suspension was observed, followed by 30 min of ultrasonic treatment to ensure uniform dispersion [24] and drying at 105 °C overnight. FA was mixed with distilled water for 2 h. Titanium(IV) isopropoxide (Sigma Aldrich Chemie GmbH, Steinheim, Germany) was diluted with ethanol (Chimreactiv, Bucharest, Romania) for a higher hydrolytic activity and dropwised slowly over a mixed suspension of FA and ultrapure water under a magnetic stirrer at 500 rpm for 3 h. The system was left at room temperature for growing (72 h), dried at 80 °C for 2 h, and calcinated at 400 °C for the next 4 h to strengthen the bond between TiO₂ and FA in a muffle furnace while the temperature was increased by 5 °C/min in order to prepare the nanocomposite FA-TiO₂.

3.2. Materials Characterization

3.2.1. Scanning Electron Microscopy

The morphology of the obtained composites was investigated by Scanning Electron Microscopy using a FEI Quanta FEG 250 (Thermo Fischer, Waltham, MA, USA).

3.2.2. Wavelength Dispersive X-Ray Fluorescence Spectroscopy (WDXRF)

WDXRF spectroscopy was applied to determine the elemental composition of studied samples, both raw-materials, and prepared composites.

The Supermini 200 WDXRF spectrometer (Rigaku, Tokyo, Japan), a benchtop instrument equipped with a Pd-anode X-ray tube (50 kV, 4 mA, 200 W) as excitation source with a 3-position crystal changer: LiF (200) for heavy elements (Ti–U) and PET and RX-25 for light elements (O–Mg and Al–Sc), was used for detecting the fluorescence radiation. The instrument offers a detection limit in the range of 1 ppm to 10 ppb.

Powdered samples were prepared as pressed pellets under a pressure of 250 kN (Testchem, Radlin, Poland), with Boreox binder (Fluxana, Bedburg-Hau, Germany), and then analyzed under vacuum in a gas atmosphere of P10 mixture (90% Ar–10% CH₄), so that stable detection conditions were ensured and good signal-to-background ratios were maintained.

3.2.3. X-Ray Diffraction (XRD)

Data acquisition for studied powders placed in glass sample holders was performed with the Ultima IV diffractometer (Rigaku, Tokyo, Japan) using monochromatic Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) from a fixed anode X-ray tube operated at a voltage of 40 kV and a current of 30 mA. Diffractograms were recorded for the angular 2-theta range of 10–90 degrees, in Bragg–Brentano geometry, in the continuous scan mode at a speed of 1 degree/min and with a step width of 0.02 degrees. The crystal microstructure analysis was performed using the functionalities of PDXL software version 2.2 and ICDD database PDF5+ version 2024.

3.2.4. Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectra of studied samples were recorded using a Vertex 80 infrared spectrometer (Bruker, Ettlingen, Germany) in the wavenumber range from 4000 cm^{−1} to 400 cm^{−1}, with 32 scans per sample and a resolution of 4 cm^{−1}. Attenuated total reflection (ATR) was used as the sampling technique, so that samples were directly measured without further preparation. The instrument is equipped with a diamond ATR crystal with low refractive index. Spectra recording and processing were performed using the instrument's specialized OPUS version 8.7 software.

3.2.5. Raman Spectroscopy

Raman spectra were recorded at 795 nm on a Xantus 2 spectrometer (Rigaku, Tokyo, Japan) in the wavelength range of 200–2000 cm^{-1} with a spectral resolution of 5–7 cm^{-1} . The total exposure time to collect the Raman spectra was 2500 milliseconds, and the applied laser power was 50 mW.

3.2.6. Point of Zero Charge

The point of zero charge is a significant physicochemical parameter since it shows the pH at which the adsorbent's surface will have zero net charge and was estimated by potentiometric titration. All the experiments were run by adding 0.02 g of each sample to 100 mL NaOH 0.1 M, followed by titration using HNO_3 0.1 M. Measurements of the pH were done after dropping HNO_3 , and equilibrium was reached. pH was measured with a multiparameter Hanna HI6000 (Hanna Instruments, Cluj-Napoca, Romania). PZC was estimated from the pH/ HNO_3 experimental curve derivative.

3.2.7. Leaching Test

The leaching test was carried out in accordance with SR EN 12457-2/2003 [35] and CEN/TR 16192:2020 [36] standards. The method involved bringing the waste into contact with distilled water (leachant) at a ratio between leachant and solid sample L/S of 10:1 and keeping it in contact for 24 h. After this period, the leachate was separated from the solid phase (using a filter with 0.45 μm porosity) and analyzed via ICP-EOS using an AVIO 500 equipment (Perkin Elmer, Shelton, CT, USA).

3.3. Photocatalytic Tests

The photo oxidation processes were carried out in the laboratory reactor of volume 0.4 L equipped with a UV lamp (Heraeus Group, Hanau, Germany). Inside the reactor, a low-pressure UV lamp was placed, emitting UV radiation at a wavelength $\lambda = 320\text{--}550$ nm with a power of 15 W. To keep the temperature constant at 22 ± 1 $^{\circ}\text{C}$, the lamp was cooled with water. Air was constantly supplied to the reactor chamber to mix the contents of the reactor and to provide oxygen, which is essential for the photocatalytic process. The reactor was equipped with a magnetic recirculation system, which pumped the reaction mixture through the attached side arm, as shown in Figure 9.



Figure 9. Experimental photocatalytic reactor setup.

4. Conclusions

TiO₂ and FA-TiO₂ composites were synthesized using a sol–gel method. All catalysts were characterized by means of SEM, XRD, and X-ray fluorescence, IR, and Raman spectroscopy.

Photocatalytic tests were performed using real wastewater with initial COD in the domain 244.4–334.4 mg O₂/L.

The 90%TiO₂-10%FA showed the best results (76.67% COD removal efficiency) but good ones were also obtained for 80%TiO₂-20%FA and 70%TiO₂-30%FA (58.00% and 56.79% COD removal efficiencies) at an optimum photocatalyst dose of 400 mg/L.

The results showed that FA-TiO₂ composites with FA content up to 30% are representing promising low-cost materials to be used for real municipal wastewater treatment.

The advantage of incorporating FA is therefore not photocatalytic superiority, but a combination of:

- Waste valorization/circular economy. FA is a by-product and could be classified as hazardous under certain regulatory frameworks; uncontrolled landfilling poses ongoing leaching and dust-dispersion risks. Incorporating FA into the composite immobilizes it within a stable matrix and diverts it from disposal, converting a liability into a functional material.
- Precursor cost reduction. Replacing a fraction of the Ti(OiPr)₄ precursor, which is the dominant cost driver in sol–gel TiO₂ synthesis, with a free or low-cost industrial waste stream lowers material cost per unit of catalyst produced, without a proportional loss in performance.
- Scalability. FA is generated in large, continuous volumes by thermal power plants, offering a more scalable and consistent feedstock than relying solely on synthetic TiO₂ precursors for large-scale water treatment applications.

While this study establishes the photocatalytic efficacy of FA-TiO₂ composites for organic load removal from real municipal wastewater, the reusability and long-term stability of the composite across multiple treatment cycles were not evaluated here and represent an important direction for future research, particularly for assessing the material's viability for practical, large-scale wastewater treatment applications.

Author Contributions: Conceptualization, M.A.C. and L.A.C.; methodology, M.A.C.; validation, M.A.C., I.A.I., F.D.C., C.M.N., M.B. and A.I.G.; formal analysis, L.A.C.; investigation, M.A.C., I.A.I., F.D.C., C.M.N. and A.I.G.; data curation, M.A.C.; writing—original draft preparation, M.A.C., M.B. and L.A.C.; writing—review and editing, M.A.C., M.B. and L.A.C.; visualization, C.M.N. and M.B.; supervision, M.A.C.; project administration, M.A.C. All authors have read and agreed to the published version of the manuscript.

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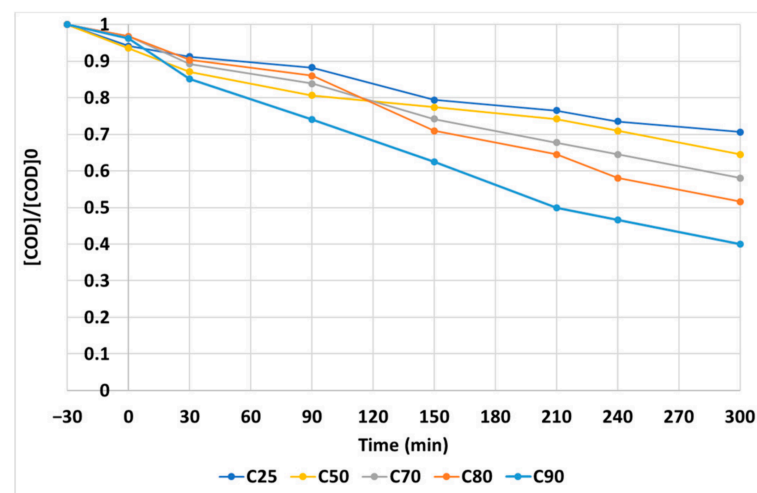
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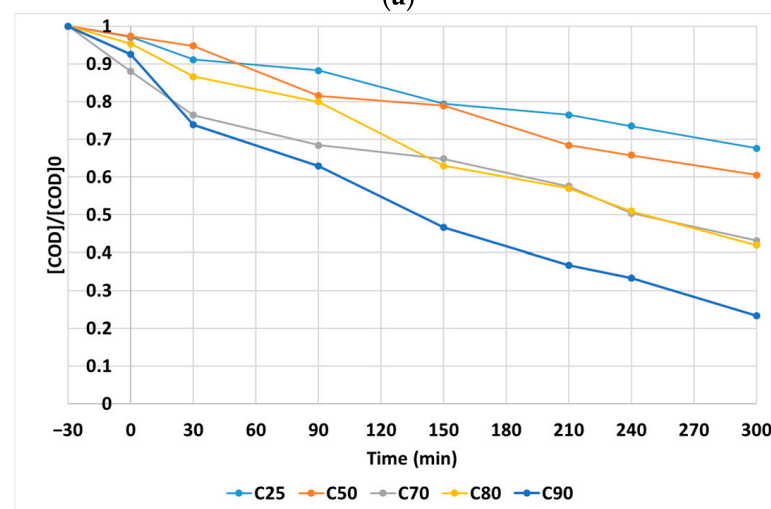
Appendix A

Table A1. Characterization of real municipal wastewater used.

Parameter	M.U.	Value
pH	unit	6.85
Conductivity	mS/cm	2.14
COD	mgO ₂ /L	284.5 ± 49.9
TDS	mg/L	793
TSS	mg/L	34
Ammonium	mg/L	0.48
Nitrate	mg/L	0.64
Nitrites	mg/L	0.07
Total Phosphorus	mg/L	6.14
Chlorides	mg/L	205.62
Extractable substances	mg/L	3



(a)



(b)

Figure A1. Cont.

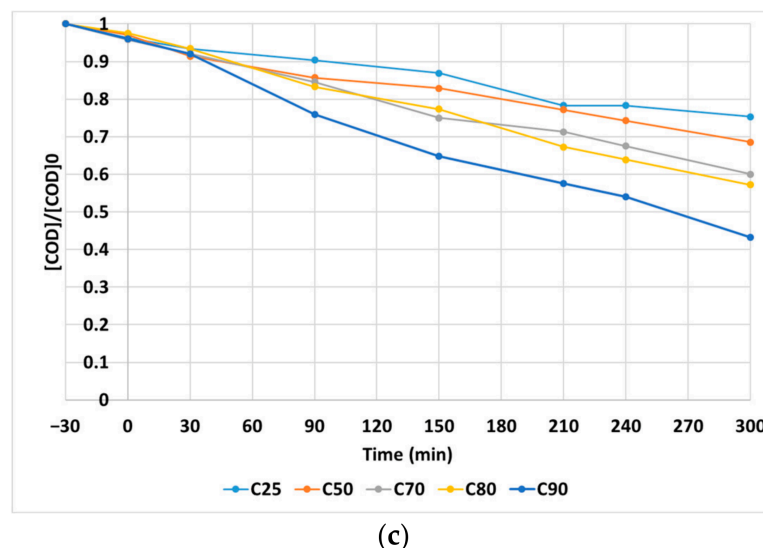


Figure A1. Normalized profile of COD variation during the photocatalytic tests for catalyst doses of (a) 200 mg/L; (b) 400 mg/L; (c) 600 mg/L.

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