**AGRO AND INDUSTRIAL RESIDUES: POTENTIAL RAW MATERIALS FOR PHOTOCATALYST DEVELOPMENT**

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**Abstract**. Agroindustrial waste (exhausted bark acacia) and Ziegler–Natta catalyst slurry waste (containing Ti and Mg) from an industrial petrochemical plant were employed as supports for photocatalysts. TiCl4 was used as the titanium dioxide precursor in the preparation of the photocatalysts. The morphology and chemical composition of the catalysts were determined by Scanning electron microscopy - energy dispersive X-ray spectroscopy (SEM-EDX) and the X-ray photoelectron spectroscopy (XPS). The band-gaps were determined by using UV diffuse reflectance spectroscopy (DRS-UV). Multiscale structural characterization, pore analysis and specific surface area were determined by small-angle X-ray scattering (SAXS) and nitrogen adsorption-desorption at -196ºC. Zeta potential (ZP) measurements were carried out to verify the stability of catalyst suspensions. The prepared photocatalytic systems (catalyst with support) were evaluated for the photodegradation of phenol. Among the tested systems, the greatest percentage of phenol degradation was 68.4 % under UV-Vis radiation. Under the same conditions, the commercial P25 catalyst achieved 43.8 % degradation. The waste derived photocatalysts allowed five reuses without losing catalyst activity, showing the applicability of recycling waste material into stable catalysts with comparable activity to the industrial standard P25.

*Keywords:* Photocatalyst; TiO2; agroindustrial residue, industrial residue; phenol.

**1. INTRODUCTION**

*Acacia mearnsii* (black wattle) is an important tree in the *Fabaceae* (*Leguminosae*) family with high productivity and fast adaptation to different environmental conditions. The major commercial plantations, aimed primarily at the production of wood, coal and tannins, are located in eastern and southern Africa, India and southern Brazil [1,2]. The bark from *A. mearnsii* is most commonly used as a raw material in the extraction of tannin substances worldwide, especially for phenolic type resins and wood adhesives. Efforts have been made to develop wood adhesives [3-5], composites [6], foams [7-10] or gels [11-13] from condensed tannins. Tannins have also been applied in the production of volatile oils [14], as inhibiters in the growth of toxic species [15], as adsorbents for pollution control of industrial effluent [16,17], and as flocculants [18,19].

In parallel, modern industrial activities have left widespread hazardous pollution in soil and water across the globe. One of the most troublesome groups of pollutants is persistent organic pollutants (POPs) [20–22]. The presence of these compounds in the environment causes considerable pollution and serious health-risk issues [23]. The physical and chemical properties of wastewater vary depending on the location, the rock types with which it is in contact and the type ofhydrocarbons. The most significant pollutants in wastewater are oil and grease, dissolved salts and poly-aromatic hydrocarbons (e.g., phenol and its derivatives). Phenol and phenolic compounds are known as human carcinogens and are of considerable health concern, even at low concentrations [24,25].

The treatment of industrial wastewaters for the removal of organic compounds is an important aspect of environmental technology. Conventional wastewater treatments cannot usually eliminate many of these pollutants [26]. Advanced Oxidation Processes (AOPs) have been presented as an alternative to conventional methods, and these processes are based on the chemical, photochemical and photocatalytic production of hydroxyl radicals (OH•), which are oxidizing agents. AOPs have proven to be a promising alternative to conventional wastewater treatments given that they imply an important reduction in operational cost [27-29]. Among the AOPs, photocatalysis is a light induced catalytic process that reduces or oxidizes organic molecules through redox reactions activated via photo-excited charge carriers [30,31].

Different approaches, such doping, semiconductor coupling, surface sensitization, increasing crystal defects and surface modification, have been reported to produce visible light active photocatalytic materials from parent wide band gap UV active semiconductors [32,33]. Elements commonly used in photocatalytic materials can be found in industrial wastes, which may then serve as precursors for the production of heterogeneous photocatalysts [34-36].

In this context, we investigated the potential of heterogeneous photocatalysts prepared from agroindustrial and petrochemical industrial waste, a sample of activated carbon was prepared from the carbonization of black acacia (*Acacia mearnsii*) and treated with phosphoric acid for use in the preparation of the catalysts with varying surface area and complexity. These photocatalysts were then applied for the degradation of phenol in water under UV-vis irradiation.

**2. MATERIALS AND METHODS**

* 1. *Materials*

One residual Ziegler-Natta catalyst slurry (Ti-based polymerization catalyst) from a petrochemical plant was employed for the preparation of the photocatalysts. Agroindustrial waste of the exhausted bark acacia, derived from a tannin extraction process black acacia (*Acacia mearnsii*), was used as the raw material for the preparation of activated carbon. TiCl4 (Merck) was used as precursor for the preparation of the TiO2 component of solid catalysts. Phenol (C6H6O, from BDH ANALAR Company) was employed as the model pollutant for the degradation tests. H3PO4 solution was prepared by a suitable dilution with deionized water from the 85% H3PO4 reagent (Dinâmica). Deionized water was used for the preparation of solutions employed in the catalytic tests.

*2.2 Synthesis of activated carbon (AC)*

The sample of activated charcoal was prepared by carbonization and activation of organic substances, mainly of plant origin [37-39]. The bark was initially dried in an oven (DeLeo) at 105○C for 24 h. Then, 10 g of the dried bark was soaked with 35% H3PO4 at the impregnation ratio (the mass ratio of H3PO4 to exhausted bark (EB) acacia) of 2:5 and placed in contact for 12 h at room temperature. Thereafter, the impregnated bark was pyrolyzed in a tubular furnace under nitrogen flow (100 mL min−1) at the ramping rate of 15 ○ min−1 to a final temperature of 500 ○C, which was maintained for 1 h. The resulting sample was cooled to room temperature, washed several times with distilled water to the pH 6-7 and dried for 6 h (105 ○C). Solids were sieved (>60 mesh) and identified as AC-EB.

*2.3 Preparation of the photocatalysts*

In a typical procedure, 3 mL of TiCl4 was added to 0.5 g of impregnated bark acacia or dried bark and stirred for 90 minutes, followed by grinding (in mortar pestle) and uniformity (12 mesh). Other prepared samples were as follows: (i) TiCl4 (3 mL) with impregnated bark (0.5 g), (ii) AC-EB (0.5 g) or TiCl4 (3 mL) with impregnated bark (0.5 g), (iii) AC-EB (0.5 g) and (iv) petrochemical residue (3 mL). The resulting powders were annealed in a muffle furnace at 450oC for 4 h. The labels employed are described in Table 1.

**Table 1.** Supported photocatalysts prepared with TiCl4

|  |  |
| --- | --- |
| Sample | Label |
| TiCl4 + exhausted bark acacia | Ti1 |
| TiCl4 + impregnated bark | Ti2 |
| TiCl4 + impregnated bark + AC-EB | Ti3 |
| TiCl4 + impregnated bark + AC-EB + petrochemical residue | Ti4 |

*2.4 Catalyst Characterization*

SEM-EDX measurements were conducted using a JEOL model JSM 5800 operating at 20 kV. The samples were coated with a thin layer of conductive carbon by using a sputter coater. The specific surface area, pore diameter and pore volume of the samples were calculated from nitrogen adsorption/desorption measurements performed on a Micromeritics Gemini 2375 instrument. The energy band gap was determined by diffuse reflectance spectroscopy (DRS-UV) in a UV-Vis spectrophotometer (Cary 100 Scan Spectrophotometers) equipped with an integrating sphere with a diameter of 60 mm using BaSO4 as the standard, by plotting (F(R)hν)2 vs hν where the band-gap value was determined by measuring the intersection of the tangent of the absorption edge with the x-axis [40].

The zeta potential (ζ) was measured on a Malvern Zetasizer® nanoZS-style instrument. XPS measurements were undertaken using a KRATOS XSAM 800 instrument equipped with an energy analyzer. The X-ray source employed was an Al Kα (hν 1,486 eV) generated from an aluminum anode operating at the emission voltage of 15 kV and 5 mA. All spectra were referenced by setting the hydrocarbon C 1s peak to 285.0 eV to compensate for residual charging effects. The small angle X-ray scattering (SAXS) analyses were performed at the SAXS line D11A at the National Synchrotron Light Laboratory (LNLS, Campinas, Brazil) using the routine evaluation Irena [41] implemented in Igor Pro (WaveMetrics, Portland, USA) software [42].

*2.5 Photocatalyst Tests*

Photocatalytic studies were performed in a stirred tank reactor (STR), reactor details have been previously reported [43]. The STR was used for all experiments, and for slurry experiments, the STR was fitted with a blank borosilicate glass window. The catalyst suspension containing the phenol was added to the STR (200 mL) and stirred with the propeller 1500 rpm with oxygen sparging (1000 mL min-1) throughout the experiment. The STR was irradiated using a 1000 W Xe lamp at a fixed distance of 16.4 cm from the borosilicate glass window to match solar UV irradiance. The reaction temperature was maintained at 20 ± 2 ºC by continuous water circulation in the outer jacket of the STR. A blank phenol solution (without catalyst) was used as photolytic control. Before the lamp was turned on, the suspension containing the phenol solution and the photocatalysts was stirred in the dark for 60 min to attain adsorption equilibrium. Then, the lamp was switched on, and an aliquot of the sample solution (5 mL) was withdrawn from the reactor at regular intervals (0, 20, 40, 60, 80, 100 and 120 min). The obtained sample was filtered (Millex® Syringe driven Filter) to achieve the separation of catalyst particles from the samples prior to further analysis. To determine the concentration of phenol, solution absorbance was measured using a PerkinElmer Lambda 35 spectrophotometer at the wavelength of maximum absorbance of the target molecule (270 nm for phenol). The absorbance was related to the concentration of the phenol through a calibration curve: Abs = 0.0456 C (mg L−1) (R2= 0.9975; N = 5). All photocatalytic tests were performed in duplicate (with an error value lower than 5%).

**3. RESULTS AND DISCUSSION**

*3.1 Catalyst characterization*

Figure 1 shows the scanning electron microscope (SEM) images collected for the native bark acacia (Fig. 1a), activated carbon prepared from the chemical treatment of exhausted bark with H3PO4 and the use of N2 in the burning process (Fig. 1b), impregnated bark acacia with H3PO4 (Fig 1c) and Ti-samples. The images provide insight on the morphology and composition of the surface of the catalysts. Comparing the images of the native material, impregnated bark and activated carbon demonstrates that all the samples have an uneven surface, showing the presence of heterogeneous and disorderly grooves, similar to a sponge. When TiCl4 is loaded onto these materials, small particles can be observed dispersing on the surface of the sample (Fig. 1d–g). Moreover, regarding the combination between these agroindustrial and petrochemical materials with TiCl4, the size of the particles in the composites increased gradually, providing greater surface area to the material (27.3 to 562.30 m² g-1).

EDX analysis indicated that the composition of the surface of the photocatalysts (example sample Ti4) included O, Al, Mg, Si and Ti. Furthermore, the presence of carbon on the particle can also be observed. A complete elemental analysis of the resulting supported catalysts is shown in Table 2.

**Table 2.** The chemical composition of the Ti-samples in terms of atomic ratio determined by SEM-EDX

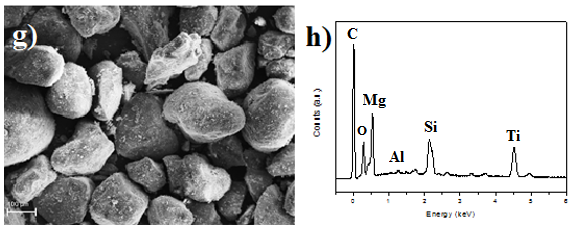
|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Catalyst** | **% C** | **% Si** | **% Ti** | **% Mg** | **% Ca** | **%Al** |
| Native bark acacia | 59.12 | 0.50 | - | - | 0.05 | - |
| AC-EB | 62.30 | 0.0 | - | - | 0.05 | - |
| Impregnated bark acacia | 60.03 | 0.50 | - | - | 0.05 | - |
| Ti1 | 59.76 | 0.50 | 0.04 | - | - | - |
| Ti2 | 59.45 | 0.50 | 0.05 | - | - | - |
| Ti3 | 59.43 | 0.50 | 0.05 | - | - | - |
| Ti4 | 59.36 | 0.50 | 0.44 | 0.83 | - | 0.01 |

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**Figure 1.** SEM images of (a) exhausted bark acacia native, (b) activated carbon from exhausted bark, (c) impregnated bark acacia, (d) Ti1, (e) Ti2, (f) Ti3, and (g) Ti4 sample with its corresponding EDX spectrum (Ti4) (h).

Figure 2 shows typical isotherms of the adsorption/desorption of N2 at 77 K, which provides information about pore size and structure. The isotherms are type IV sorption with a H3 hysteresis loop, according to IUPAC classification [44]. This classification indicates the existence of mesoporous structure in the corresponding materials. The adsorption branch exhibits three distinct regions, corresponding to monolayer-multilayer adsorption, multilayer adsorption on the outer particle surfaces and capillary condensation at relative pressures in the range from 0.6 to 0.9 for all the isotherms. The Ti4 sample showed the highest specific surface area and pore volume. For photocatalysis, one relevant strategy to enhance degradation is to enhance the surface area of the catalyst to promote availability of sites for adsorption of the pollutant. In addition, a significant pore volume to the catalysts can allow diffusion of the pollutant to the catalyst center [45]. Thus, an idealized catalyst should be stable and possess a high surface area with a three-dimensional mesoporous structure.



**Figure 2.** Isotherms for adsorption/desorption of N2 of samples prepared with TiCl4 and industrial and agroindustrial wastes.

XPS measurements were performed, and a summary of these results is reported in Table 3. XPS spectra of different regions were obtained for selected samples; all the spectra were calibrated with the C 1s peak at 285 eV, attributed to adventitious surface carbon. Spectra of Ca 2p and Al 2p regions are not shown due to the lower content of these elements in all the analyzed samples. In the spectra a peak of Si 2p is observed, in addition the Ti4 sample also showed the peaks of Ti 2p and Mg 1s.

**Table 3.** XPS survey data for the three resulting supported photocatalyst prepared with agroindustrial waste (exhausted bark acacia) and Ziegler–Natta catalyst slurry (bearing Ti and Mg) from an industrial petrochemical plant

|  |  |  |  |
| --- | --- | --- | --- |
| **Samples** | **Peak designation** | **Binding Energy (eV)** | **FWHMa (eV)** |
| TiO2 | Ti 2p3/2 | 458.90 | 3.0 |
| Ti1 | Si 2p | 103.3 | 3.7 |
| Ti2 | Si 2p | 103.1 | 3.5 |
| Ti3 | Si 2p | 102.8 | 3.2 |
| Ti4 | Mg 1s | 1304 | 5.9 |
|  | Si 2p | 103.5 | 5.0 |
|  | Ti 2p3/2 | 460.5 | 3.8 |

a Full width at half maximum intensity

According to Table 3, the Ti 2p peaks appeared at approximately 460.4 ± 0.1 eV (Ti 2p3/2) in the Ti4 samples. This indicates that the Ti species primarily exist as Ti4+ [46]. In addition, the 1304 eV Mg 1s peak results from Mg-O bonding, indicating that Mg may replace the Ti site in the SiO2 lattice [47]. Moreover, the FWHM values of the prepared supported photocatalysts are larger than that of commercial TiO2, suggesting an increased heterogeneity of the generated supported species [48].

UV–vis diffuse reflectance spectra (DRS) were collected prior to the assessment of the photo-degradability performance of each photocatalyst. It is known that the optical properties of a photocatalyst and its catalytic performance are closely related [49]. Conversely, the Ti2, Ti3 and Ti4 samples all possess smaller *E*g values (3.09–2.55 eV), as listed in Table 4. In all cases, the values were lower than that reported for P25 (ca. 3.34 eV) [50]. Notably, the Ti4 sample exhibited the lowest *E*g value among the prepared photocatalysts, possibly due to the interactions of TiCl4 with the impregnated bark, activated carbon from exhausted bark and petrochemical residue resulting in modification if the titania.

Zeta potential (ζ) measurements were used to verify the stability of the suspensions of support and catalyst, and the surface potential was measured to determine their influence on the phenol adsorption of the studied particles. The zeta potentials of Ti-samples prepared with petrochemical and agroindustrial wastes are displayed in Table 4 along with results of all physicochemical measurements. The observed zeta potential behavior results from the combined effects of all the precursors added to the system and thermal processing conditions. There was trend of increasing value (modulus) of the zeta potential, moving from Ti1 to Ti4 mirroring the complexity of the mixtures utilized in synthesis. Because higher absolute values of zeta potentials indicate higher suspension stability [51] and thus reduced particle agglomeration processes. The specific surface area of the colloidal Ti-samples was observed to follow a trend directly proportional to the absolute value of the zeta potential.

The SAXS technique was used for photocatalyst characterization to elucidate the structure of these multi-scale materials. In the present study, the SAXS curves of these materials have a structure formed by the organizational levels composed of a Guinier region and a potency law. The former provides an estimation of the Guinier radius of gyration (Rg), while the latter provides details about the organization of the system. Figure 3 shows the resulting scattering curves of the investigated systems.



**Figure 3.** SAXS curve for samples photocatalysts prepared.

According to Figure 3, the unified set of SAXS data reveals that the catalysts are arranged in a multi-scale structure that consists of three organizational levels. By analyzing Level 1, which is located in the q region greater than 3 nm-1, the radius of gyration (Rg) of the primary particles can be determined. Level 2, which is located in the q region between 0.1 and 4 nm-1, can be used to determine the radius of gyration (Rg) of the secondary particles. Level 3, which is located in the q region below 0.1 nm-1, provides information on the organization of these particles, i.e., on the structure of fractal clusters (secondary particles) resulting from the aggregation of primary particles [52].

The structure of the clusters of primary particles that constitute Level 3 can be obtained by analyzing the power law exponent (P) of the scattering curve. If the exponent of the power law is between 1.0 and 3.0, the particles have a mass fractal structure. If P is between 3.0 and 4.0, the particles have a fractal surface. In the case of P equal to 4.0, the particles have a dense core and a uniform surface [53]. In the present study, the SAXS curves for all of the systems revealed the presence of three distinct organizational levels. The results obtained from the unified set of SAXS curves for the prepared photocatalyst samples are presented in Table 4.

As shown in Table 4, taking into account Level 1, there was a decrease in the Rg of the catalyst preparations. The Rg of the primary particles of the photocatalysts ranged between 0.23 and 1.26 nm. The highest value of Rg (1.26 nm) was observed for Ti4, while the lowest (0.23 nm) was observed for Ti1. Comparing the Level 3 values of the systems, a decrease was observed in P after the addition of each material, suggesting that a more ramified system has formed. Regarding the organization of the particles in terms of P, values between 2.0 and 3.7 were observed. For Ti2, Ti3 and Ti4, the formation of particles with less condensed structures (mass fractals) could be observed because the P values lay between 2.0 and 2.9. For the Ti1 sample, the formation of particles with characteristics of a fractal surface was observed because the P value was 3.7. It is apparent that there is an increase in the particle size (increase in the radius of gyration), most likely due to the interaction of the TiCl4 with each material that was added, which in turn resulted in more aggregated structures consistent with the SEM images, i.e. increasingly complex mixtures going Ti1 🡪 Ti4 resulting in increasingly higher surface area materials (BET) with higher fractal numbers (SAXS), resulting in more complex surfaces with generally higher zeta potentials and therefore greater stability.

**Table 4.** Results of the surface area (SBET), pore diameter (Dp), pore volume (Vp), band gap energy (Eg), absorption wavelength (λ), zeta potential (ZP) and SAXS parameters (Rg = radius of gyration; Rp = radius of particle; α = prefactor specific) of the Degussa P25 and photocatalysts prepared from agro and petrochemical residues

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Catalyst** | **Degussa P25** | **Ti1** | **Ti2** | **Ti3** | **Ti4** |
| SBET (m² g-1) | 56 | 27.3 | 28.3 | 106.5 | 562.30 |
| Dp (nm) | 4.8 | 13.15 | 16.76 | 28.00 | 32.95 |
| Vp (cm³ g-1) | 0.07 | 0.07 | 0.09 | 0.17 | 0.24 |
| λ (nm) | 371.2 | 365.8 | 401.3 | 454.2 | 486.3 |
| Eg (eV) | 3.34 | 3.39 | 3.09 | 2.73 | 2.55 |
| ζ (mV) | -3.6 | -10.6 | -17.9 | -20.7 | -28.4 |
| Rg1 (nm) | 0.33 | 0.23 | 0.68 | 0.99 | 1.26 |
| Rg2 (nm) | 0.43 | 7.28 | 7.30 | 11.88 | 13.27 |
| α | 4.00 | 3.7 | 2.9 | 2.9 | 2.0 |

Therefore, by combining these factors it appears the addition of petrochemical waste can be helpful in producing a more complex catalysts which result in superior physiochemical properties compared to less complex catalyst mixtures

*3.2 Photocatalytic Activity*

The photocatalytic activity of the Ti photocatalysts and P25 was assessed via the degradation of phenol (initial concentration 10 mmol L-1) under UV-Vis irradiation. No significant degradation of phenol was observed under irradiation in the absence of photocatalyst. Figure 4 shows the photocatalytic activity and the kinetics of the degradation reaction fitted with a pseudo-first order reaction, and the apparent rate constant *k* (min-1) was determined. In order to correlate to other work, the rate of phenol degradation with Evonik Aeroxide P25 was also determined under the same conditions. As shown in Figure 4, the Ti4 sample showed the best photocatalytic activity under UV-Vis irradiation with *k* = 9.3 x 10-3 min-1. The order of efficiency for the catalysts was Ti4 > Ti3 (*k* = 5.8 x 10-3 min-1 ) > P25 (*k* = 4.3 x 10-3 min-1) > Ti2 (*k* = 2.7 x 10-3 min-1) and Ti1 (*k* = 9 x 10-4 min-1).



**Figure 4.** Photocatalytic degradation of phenol under UV-Vis radiation with the insert shows the rate constant evaluated for the different photocatalysts (Ccatalyst = 50 mg L-1, Cphenol = 10 mmol L-1, T = 30 °C and natural pH).

The addition of photocatalyst modifers including; impregnated bark, activated carbon from exhausted bark and petrochemical residue, resulted in the photocatalytic degradation rate gradually increasing according to the increasing complexity (due to the addition of each material) of the photocatalyst. From Ti1 to Ti4, both the SBET value and adsorption capacity increased stepwise, and the photocatalytic activity increased following this trend. The relationship between surface area and activity is illustrated in figure 5a. Conversely, the photocatalytic activity and band gap energy showed an inverse trend in these preparations. Such that the Ti4 sample with an Eg of 2.55 eV presents the highest rate constant, while the sample Ti1 (3.39 eV) presents the lowest rate value. Illustrated in Figure 5b.



(a)



(b)

**Figure 5.** Correlations between the rate constant under UV-Vis radiation and (a) BET surface area and (b) band gap energy.

The improvement in the photocatalytic activity of the Ti-samples are due to the physicochemical properties induced by interaction between the TiCl4 with black acacia and the petrochemical wastes during synthesis. To understand the contributions of the most significant physiochemical properties of the catalysts differences in surface area and optical band gap were rationalized to photocatalytic testing with phenol. Clear trends were observed where in increasing the surface area or increasing the absorbed radiation between catalysts preparations leads to some catalysts Ti3 and T4 which give better activity than the commercial P25. We determined the BET surface area of Ti1 and Ti4 by a nitrogen adsorption-desorption isotherm measurement, and the results are approximately 27.3 and 562.3 m2 g-1, respectively. There is a significant improvement in the surface area of the samples due to the introduction of activated carbon from exhausted bark (AC-EB) and petrochemical residue. This increased surface area will in turn increase the adsorption of phenol molecules onto the surface of the photocatalyst relative to other preparation methods for Ti-samples.

**4. CONCLUSION**

It is possible to recycle industrial and agrochemical waste into support material for catalysts. In this work we show that when increasingly complex mixtures of waste are used for support materials (samples Ti1-Ti4). The complexity of the resulting catalysts geometry, in terms of fractal dimensions, porosity and ultimately surface area increase with increasing complexity of support. In turn the increased surface area induced in catalysts using waste material as a support was shown to lead to an increase in the rate of phenol removal. In comparison to the photocatalytic standard material two of the highest surface area photocatalyst materials Ti3 and Ti4 showed higher rates of phenol removal as these materials had a higher surface area than p25. This work shows the potential for waste products to be repurposed as catalyst supports to increase the activity of known catalysts though extending the surface complexity and surface area.

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**FIGURE CAPTIONS**

**Figure 1.** SEM images of (a) exhausted bark acacia native, (b) activated carbon from exhausted bark, (c) impregnated bark acacia, (d) Ti1, (e) Ti2, (f) Ti3, and (g) Ti4 sample with its corresponding EDX spectrum (Ti4) (h).

**Figure 2.** Isotherms for adsorption/desorption of N2 of samples prepared with TiCl4 and industrial and agroindustrial wastes.

**Figure 3.** SAXS curve for samples photocatalysts prepared.

**Figure 4.** Photocatalytic degradation of phenol under UV-Vis radiation with the insert shows the rate constant evaluated for the different photocatalysts (Ccatalyst = 50 mg L-1, Cphenol = 10 mmol L-1, T = 30 °C and natural pH).

**Figure 5.** Correlations between the rate constant under UV-Vis radiation and (a) BET surface area and (b) band gap energy.

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