Evaluation of carbonaceous materials coupled with TiO_2 for the coliform bacteria removal

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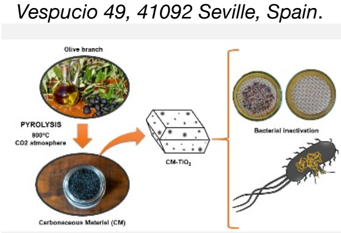

In this work a carbonaceous material (CM) was obtained by pyrolysis of olive branch pruning, this material was coupled with different loading of TiO_2 (iw. 1 and 10 wt.%). The coupled materials showed better effectiveness in the coliform bacteria removal from wastewater samples than that observed by using the bare TiO_2. The best bacteria elimination was achieved with the 1%CM-TiO_2, using this material was also possible to obtain the highest decreasing in different water quality control parameters such as pH, nitrates, chlorides and total hardness. It was also observed that the CM content did not significantly affect the effectiveness of the coupled materials.

Introduction

The improvement of heterogeneous photocatalysis based on TiO_2, still remains a global challenge today. Carbonaceous materials currently represent a good alternative to be coupled with Titania as more efficient materials focused in environmental remediation; these materials can effectively produce a synergistic effect between the photocatalytic properties of TiO_2 and the high surface area of carbonous components and its adsorption properties, thus improving the global effectiveness of the obtained materials.
The biomass is an interesting raw material to produce activated carbon [1], thus, the main objective of this work was to valorize the olive branch pruning, as CM to be coupled with TiO_2 for enteropathogenic bacteria elimination.

Material and Methods

Photocatalytic materials preparation: The CM was prepared by pyrolysis of olive branch pruning, at 800°C for 1 hour. In order to avoid the hydrophobicity in the obtained materials, the biomass was heated under CO_2 atmosphere. Before calcination, the biomass was grounding in a ball mill. Then, the CM was placed in a high-performance microwave digestion system (Milestone, Ethos ONE) and heated at 140°C for 2 hours. After cooling to room temperature, the resulting precipitate was centrifuged, washed five times with deionized water, and dried at 100°C overnight.
Inside of this reactor, TiO_2 was also synthesized using titanium tetraisopropoxide and HF, in a tetraisopropoxide:HF of 24/4 (v/v) ratio. The CM loading was 1 and 10% by weight, considering a final yield of 100%.

Photocatalytic materials characterization: All the materials synthesized were analyzed by different techniques, such as:
N_2 physisorption: The specific surface area was determined in an ASAP 2010.
XRD: The diffraction patterns were determined in a PANalytical X'Pert PRO instrument, using the Cu Kα radiation (40 mA, 45 kV).
Photocatalytic activity test: Water samples taken from a local river highly polluted by domestic and industrial wastewater was selected as problem sample; which was collected following the Standard Methods for the Examination of Water and Wastewater instructions.
250 mL of the water sample was placed in a discontinuous Pyrex reactor with 1 g/L of photocatalytic material, under constant stirring the reactor was irradiated by an Osram Ultra-Vitalux lamp (300 W), light intensity: 30 W/m^2, oxygen flow: 0.84 STP L/h, and a total reaction time of 4 hours.
After treatment, the photocatalyst was recovered by filtration, and the treated water was analyzed by physicochemical and microbiological methods. All photocatalytic tests were conducted twice, with a standard deviation below 0.05. The reported values are estimated as the arithmetic average.
Chloride, nitrates and total hardness analyses were conducted in a Spectroquant® Move 100 instrument. To ensure result reproducibility, each assay was performed twice.
Microbiological analysis was carried out using the membrane filtration method Merck SM 9222B and ISO 9308 part 1. Chromocult® agar was employed as a culture medium for coliform bacteria, the bacteria concentration is reported as Colony Forming Units (CFU) per 100 mL of water sample.

Results and Discussion

By physicochemical characterization, was possible to determine that, the specific surface area of the CM significantly decreases after its coupling with TiO_2, which is mainly due to the low S_{BET} of this semiconductor. Thus, the starting CM showed 486.6 m^2/g of surface area, after coupling this value decreased to 145.6 m^2/g and 143,1 m^2/g for the samples modified with 1% and 10%, respectively.

By XRD were only identified diffraction patterns characteristic of anatase phase of Titania, thus indicating a good coupling of this oxide with the CM. Table 1, summarizes the results obtained before and after the treatment of the water sample with the different photocatalytic materials. As it can be observed in this table, the starting water sample is highly polluted by bacteria and inorganic compounds.

Firstly, a blank reaction was carried out only under UV-Vis light without photocatalyst, after 4 hours of irradiation the bacteria content significantly decreased; which is mainly due to the bactericidal effect of this radiation [2]. Some parameters such as chlorides and total hardness also decreased after photolysis reaction.

The TiO_2 photocatalytic treatment significantly improves the bacteria removal, thus, leading obtain only 2 CFU/100mL of *E. Coli* remaining after 4h. The effectiveness observed is associated with the oxidative stress on membranes and intracellular components caused by reactive oxygen species (ROS), thus leading to DNA damage [3].

The photocatalytic material prepared with 1% of CM and TiO_2 (1%CM-TiO_2) presented the best bactericidal performance; thus, by using this material was possible to achieve the total elimination of *E. Coli*, *Citrobacter freundii, Enterobacter aerogenes*, total coliforms and other gram negatives bacteria. This behavior can be due to the synergistic effect between the good photocatalytic properties of TiO_2 and the surface area of CM, which led the highest surface available for the interaction of bacteria and organic and inorganic pollutants on the photocatalytic material; thus, also leading to the best bacteria and organic pollutant elimination.

Finally, it is also important to note the slight detrimental effect on the photocatalytic effectiveness after the increase in the CM loading to 10%. This is mainly associated with a possible obstruction of the TiO_2 surface with the CM particles which present the darkest color.

Table 1. Quality control parameters of water sample before and after photocatalytic treatments.

Water quality control parameters	Starting water sample	Photolysis	TiO_2	1%CM-TiO_2	10%CM-TiO_2
E.Coli (CFU/100mL)	$1.5x10^4$	15	2	0	0
Citrobacter freundii, Enterobacter aerogenes (CFU/100mL)	$8.3x10^4$	190	7	0	1
Total coliforms (CFU/100mL)	$9.83x10^4$	205	9	0	1
Other gram negatives (CFU/100mL)	$1.0x10^4$	290	11	0	1
pH	6.49	6.96	6.42	5.71	5.62
Nitrates (mg/L)	5.30	5.52	0.46	2.26	3.46
Chlorides (mg/L)	12.6	11.3	10.3	6.60	12.3
Total hardness (mg$CaCO_3$/L)	48.6	45.3	43.0	34.3	45.0

Conclusions

The coupling of TiO_2 with 1wt.% of carbonaceous material obtained by pyrolysis of olive branch pruning is a suitable strategy to improve the effectiveness of this semiconductor in the coliform bacteria removal (*E. Coli*, *Citrobacter freundii, Enterobacter aerogenes*, total coliforms and other gram negatives bacteria) from a highly polluted natural water source. An increase in the carbonaceous content had a detrimental effect on the bacteria elimination.

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