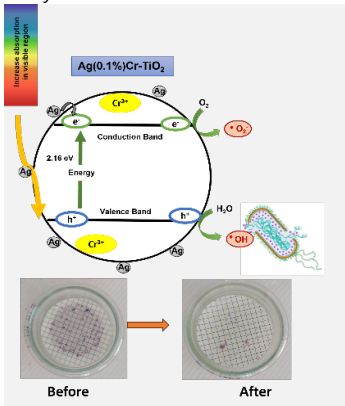
Cr-doped TiO_2 decorated with noble metals, with enhanced activity in the elimination of bacteria and yeast.

ORAL
Ph.D. Student: Yes
Journal: JECE

M. Hernández-Laverde[1,2], *B. L. Gutiérrez*[2], *J.J. Murcia*[1], *N. Morante*[3], *D. Sannino*[3], *and V. Vaiano*[3].
(1) Grupo de Catálisis. Universidad Pedagógica y Tecnológica de Colombia UPTC, Avenida Central del Norte, Tunja, 150002 Boyacá, Colombia. e-mail: monica.hernandez06@uptc.edu.co
(2) Grupo de Investigación Agroalimentaria de la Universidad Nacional Abierta y a Distancia (GIA UNAD). Escuela de Ciencias Básicas Tecnologia e Ingeniería, Sogamoso 152217, Boyacá, Colombia.
(3) Department of Industrial Engineering, University of Salerno, Via Giovanni Paolo II 132, 84084 Fisciano (SA), Italy.



In this study, coliform bacteria and yeast have been selected as target microorganisms to be eliminated with photocatalysts based on TiO_2. TiO_2 was synthesized by sol-gel method and doped with Cr, then, was modified by chemical photoreduction of Ag or Pd nanoparticles (NPs). These nanomaterials were extensively characterized, and it was found that after TiO_2 Cr-doping, the parameters of the crystal lattice slightly increased, due to the incorporation of Cr^{3+} ions into the TiO_2 lattice. A decrease in the band gap value after this modification was also observed. It was evidenced that chemical photoreduction of Ag or Pd on the Cr-TiO_2 surface favors the increase of absorption in the visible region of the electromagnetic spectrum. By using Ag (0.1%)/Cr-TiO_2 was achieved the complete elimination of *E. coli* from samples of water coming from a highly polluted river. Pd (0.5%)/Cr-TiO_2 showed the highest efficiency in the elimination of the *S. cerevisiae.*

Introduction

Water sources have been polluted with organic wastes such as dyes, oils, fertilizers, inorganic pollutants such as heavy metals, metallic compounds, salts, and enteric microorganisms as a result of anthropogenic activities [1]. This study proposes heterogeneous photocatalysis as a potential solution to this environmental problem. This treatment is based on the formation of reactive oxygen species (ROS) which are effective in the elimination of bacteria and organic matter. In order to improve the photocatalytic efficiency and to decrease the recombination of the photogenerated charge carriers, the application of metallic and non-metallic dopants, heterojunctions, and the deposition of noble metals on the surface, has been evaluated [2].

This research was focused on the evaluation of photocatalysts based on Cr-doped TiO_2, modified by Ag or Pd nanoparticles, in elimination of yeast and enteric bacteria.

Materials and Methods

Materials preparation:

Cr-TiO_2: Firstly, TiO_2: was obtained by sol-gel method, then, the amount of chromium nitrate to obtain a nominal Cr content of 0.7 wt.%. was dissolved in 50 mL of distilled water. Then, was added 12.5 mL of titanium tetraisopropoxide drop by drop, under stirring at room temperature for 10 min. This suspension was centrifuged and washed three times; and finally, it was calcined at 450 °C for 30 min [3].

Pd/Cr-TiO_2 and Ag/Cr-TiO_2: 0.1 and 0.5 wt.% of Ag or Pd were added by chemical photodeposition [3].

Photocatalyst Characterization:

X-ray diffraction analysis was performed in an Xpert Panalytical diffractometer, using the Cu Kα radiation (35 mA and 40 KV). Crystallite sizes were estimated by using the Scherrer equation. The light absorption characteristics of the photocatalysts were studied by UV-Vis DRS in a Thermo Scientific spectrometer Evolution 300. Band-gap values were calculated from Kubelka-Munk functions. X-ray fluorescence analysis was carried out in a Panalytical Minipal 2 equipment.

Photocatalytic activity test: These processes were performed in a batch pyrex reactor containing 250 mL of water sample, oxygen flow of 0.84 $L.h^{-1}$, 1g.L^{-1} of photocatalyst at 30 $W.m^{-2}$ of light intensity.

The water samples were taken from a Colombian river (geographic coordinates 5.553981, –73.350224), polluted with industrial and domestic wastewater.

The microbiological analysis was performed by membrane filtration method ISO 9308 method part 1. For the yeast elimination test, a suspension of active dry yeast *Saccharomyces Cerevisiae* Levapan® ($3.8x10^5$ number of yeast/mL) was prepared. The yeast content was determined by the ISO 21527- Part 1 method.

Results and Discussion

By XRD were identified diffraction patterns located at 25.6° 2θ and 31.0° assigned to Anatase and brookite phases of TiO_2, respectively. The calculated Anatase lattice parameters for planes (101) and (004) revealed a slight increase in the a, b

and c parameters due to the expansion of the unit cell volume compared to the bare TiO_2, indicating a lattice modification in the anatase structure arrangement, due to the incorporation of Cr ions into the TiO_2 lattice.

The UV-Vis DR spectra of the photocatalytic materials are plotted in Figure 1, as it can be observed in this figure, the incorporation of the noble metals NPs led to the absorption in the visible region of the electromagnetic spectrum, which is mainly due to the colour of the reduced metals.

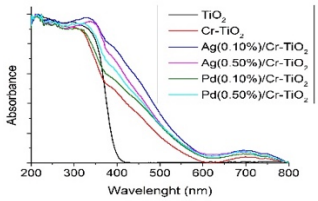


Figure 1. UV-Vis DR spectra.

Table 1. Main photocatalysts characterization results.

Photocatalysts	$D_{Anatase}$ (nm)	S_{BET} (m^2g^{-1})	Lattice Parameter(A°)		Band gap (eV)
			a=b	C	
TiO_2	7.71	107	3.69	9.33	3.22
Cr-TiO_2	7.59	113	3.73	9.41	2.15
Ag (0.1%)/Cr-TiO_2	7.68	91	3.75	9.44	2.16
Ag (0.5%)/Cr-TiO_2	8.14	92	3.75	9.44	2.12
Pd (0.1%)/Cr-TiO_2	7.66	95	3.75	9.44	2.00
Pd (0.5%)/Cr-TiO_2	7.74	103	3.75	9.44	2.03

All materials modified with Ag NPs and Pd NPs showed better photocatalytic performance in the inactivation of bacteria present in river water compared to bare TiO_2. Only with the Ag(0.1%)/Cr-TiO_2 material was achieved total inactivation of *E. coli* (Table 2). This is mainly due to the dual functionality of Ag NPs in this photocatalyst, which can act as electron traps, thus avoiding the charge carriers recombination and also can contribute with the bactericidal effect.

Table 2. Population of bacteria and yeast before and after the photocatalytic treatments

Treatment	*E. coli*	Total coliforms	Other Enterobacteriaceae	Yeasts (Estimated number /mL)
	(CFU/100mL)			
Starting sample	175454	361565	1900	380000
Photolysis	1250	8350	275	30000
TiO_2	11	246	440	2600
Cr-TiO_2	5	383	165	2400
Ag (0.1%)/Cr-TiO_2	0	16	18	1800
Ag (0.5%)/Cr-TiO_2	2	232	190	2400
Pd (0.1%)/Cr-TiO_2	7	19	265	2600
Pd (0.5%)/Cr-TiO_2	1	281	210	1000

Conclusions

Total elimination *E. coli* was achieved with Ag(0.1%)/Cr-TiO_2 and 99.71% of *S. Cerevisiae* elimination was obtained by using Pd(0.5%)/Cr-TiO_2, thus showing these photocatalytic materials as promising alternative for enteric bacteria and yeast removal.

Acknowledgments

M. Hernández-Laverde acknowledge for study grant Bicentennial Doctoral Excellence from Ministerio de Ciencia Tecnología e Innovación (Colombia). Ministerio de Ciencia, Tecnología e Innovación—Minciencias and Ministerio de Salud y Protección Social, funded Project 110991891727, Universidad Pedagógica y Tecnológica de Colombia (UPTC) Project SGI 3393 and Universidad Nacional Abierta y a Distancia (UNAD).

References

[1] F. Hernández *et al*., *Journal of Hazardous Materials*, *282* (2015) 86.
[2] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, *science*, *293* (2001) 269.
[3] D. Sannino *et al*., *Nanomaterials*, *13*, (2023). 2341.