## TIO<sub>2</sub>-LDH NANOCOMPOSITES FOR ORGANIC DYE REMOVAL FROM AQUEOUS MEDIA BY ADSORPTION AND PHOTOCATALYTIC DEGRADATION

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Layered double hydroxides (LDH) are ionic lamellar compounds known as sorbents, catalysts, anion exchangers, and drug delivery systems. Due to it's unique layered structure, adjustable band gap, large surface area, low cost, and remarkable recyclability LDH attract attention to be applied for the photocatalytic process. The combination of LDH with  $TiO_2$  caused the improvement of the photocatalytic activity of hybrid materials.

 $TiO_2$ -ZnCuAl LDH/Ag composites were applied for the removal of the anionic dye Acid Orange 7 (AO7) from aqueous solutions by adsorption and photodecomposition in neutral and alkaline medium.



XRD patterns of ZnCuAl LDH - 1; ZnCuAl MO - 2; ZnCuAl/Ag LDH - 3; TiO<sub>2</sub>/10ZnCuAl/Ag - 4; TiO<sub>2</sub>/20ZnCuAl/Ag - 5; TiO<sub>2</sub>/50ZnCuAl/TiO2/Ag - 6). LZn -ZnAl LDH structure, LCu -ZnAl LDH structure, \*- ZnO structure, a - anatase TiO<sub>2</sub>, r-rutile TiO<sub>2</sub>.



UV-vis/DR spectra (A) and Tauc plots of investigated samples: ZnCuAl LDH -1; ZnCuAl MO - 2; ZnCuAl/Ag LDH - 3; TiO<sub>2</sub>/10ZnCuAl/Ag - 4; TiO<sub>2</sub> /20ZnCuAl/Ag - 5; TiO<sub>2</sub>/50ZnCuAl/Ag - 6.

# The removal of AO7 by adsorption and by photodegradation

## Photocatalytical activity study

Sample	Adsorption, %		Photodestructi		Total removal			
	pH 7	pH1	pH 7	pН	pH 7		pH 11	
		1		11	%	mg/g	%	mg/g
blank	—	—	4.2	5.2	4.2	4.4	5.2	5.4
ZnCuAl LDH	38.4	35.8	14.6	37.6	53.0	55.5	73.4	76.8
ZnCuAl MO	99.2	90.8	_	_	99.2	103.9	90.8	95.1
ZnCuAl/Ag LDH	72.2	23.8	10.6	41.6	82.8	86.7	65.4	68.5
TiO <sub>2</sub> /10ZnCuAl/Ag	17.2	0.8	39.0	89.9	56.2	58.8	91.7	96.0
TiO <sub>2</sub> /20ZnCuAl/Ag	25.4	0	37.9	91.6	63.3	66.3	91.6	96.0
TiO <sub>2</sub> /50ZnCuAl/Ag	45.6	0	43.3	72.5	77.8	81.5	72.5	75.9
TiO <sub>2</sub> -P25	1.0	3.4	62.9	84.6	63.9	66.9	88.0	92.1

### Conclusions

ZnCuAl LDH with atomic ratio Zn:Cu:Al=3.8:0.2:1 was synthesized by coprecipitation method and used for the obtaining of calcined LDH, Ag NP-contained ZnCuAl LDH, and TiO<sub>2</sub>/ZnCuAl/Ag nanocomposites.

The adsorption of AO7 dye on LDH and its composites with  $TiO_2$  can be controllable by pH and by the modification with Ag NP. The highest total removal of the dye (99 %) at pH 7 was observed for ZnCuAl MO due to adsorption.

The photocatalytic activity of all studied materials to degrade dye under UV light greatly increased at pH 11 due to the more efficient formation of hydroxyl radicals. The highest activity in AO7 degradation under UV light among all materials studied was observed for  $TiO_2/10ZnCuA1 LDH/Ag$  and  $TiO_2/20ZnCuA1/Ag$  composites. Formation of  $TiO_2/ZnCuA1 LDH$  heterojunction allowed better separation of generated electrons and holes, which consecutively increased the efficiency of AO7 photodegradation process.

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Pseudo-first-order degradation kinetics for AO7 with: no photocatalyst - 1; ZnCuAl LDH - 2; ZnCuAl/Ag LDH - 2; TiO<sub>2</sub>/10ZnCuAl/Ag - 3; TiO<sub>2</sub>/20ZnCuAl/Ag - 4; TiO<sub>2</sub>/50ZnCuAl/Ag - 5



Evolution of the AO7 spectrum with the irradiation time in the presence of TiO<sub>2</sub>/10ZnCuAl/Ag