The Scientific Bulletin of VALAHIA University
MATERIALS and MECHANICS –Vol. 21, No. 25

DOI 10.2478/bsmm-2025-0012

EVALUATION OF SILVER-MODIFIED ZNAL-LAYERED DOUBLE HYDROXIDE COATINGS FOR PHOTOCATALYTIC SELF-CLEANING OF MORTAR SUBSTRATES

Claudiu Eduard RIZESCU [1], Ionut ZAULET [1], Anca Irina GHEBOIANU [2], Rodica Mariana ION [1,2,3]

[1] National Institute for Research & Development in Chemistry and Petrochemistry - ICECHIM, Research Group Evaluation and Conservation of Cultural Heritage, 202 Splaiul Independentei, 060021, Bucharest, Romania.
[2] Valahia University of Targoviste, Doctoral School of Materials Engineering, 13 Aleea Sinaia, 130004, Targoviste, Romania.
[3] Academy of Romanian Scientists, 3 llfov Street, 050044 Bucharest, Romania.

Email: claudiu.rizescu91@gmail.com; rodica_ion2000@yahoo.co.uk

Abstract: *The preservation of stone and mortar elements in cultural heritage structures is increasingly challenged by environmental degradation, pollution, and biological fouling. Photocatalytic coatings represent a promising approach for developing self-cleaning and pollutant-degrading surfaces. In this study, a silver-modified ZnAl-layered double hydroxide (Ag@ZnAl-LDH) was synthesized via coprecipitation and applied as a coating on mortar substrates. The structural and compositional characteristics of the prepared materials were investigated using X-ray diffraction (XRD) and wavelength-dispersive X-ray fluorescence (WDXRF). The XRD pattern confirmed the formation of a ZnAl-LDH phase (JCPDS 48-1022) with carbonate as the main interlayer anion, along with additional reflections attributed to ZnO (JCPDS 99-0111) and silver-containing species. The photocatalytic activity was evaluated through the degradation of methylene blue under natural illumination (700 W/m²), monitored via CIELAB colorimetric parameters. The results demonstrated that Ag@ZnAl-LDH coatings promote the photodegradation of organic dyes, indicating potential for developing functional, self-cleaning coatings for the protection of heritage materials.*

Keywords*: Layered Double Hydroxides, Mthylene blue, photodegradation, mortar durability*

1. INTRODUCTION

The stone elements of buildings and heritage sites located in the urban environments, are prone to degradation from a host of factors, including water-related damage, pollution, acid rains, the accumulation of airborne particles, and biological fouling. These processes not only alter the aesthetic appeal of these structures but also compromise their structural integrity. Multiple innovative mitigation strategies have been explored to preserve these cultural monuments while also enhancing their resilience, they often involve treatments with consolidants or coatings that aim to improve the material cohesion at the surface, limit the water absorption while also repelling the formation of microbiologic films. Novel strategies also involve the use of materials with photocatalytic properties that harnesses light to trigger chemical reactions that break down pollutants and organic matter on the stone's surface. This self-cleaning mechanism helps maintain both the aesthetic charm and structural health of heritage sites [1], [2].

When a semiconductor material is exposed to photons with energy equal to or greater than its band gap, it generates photo-electrons (e^-) and photo-holes (h^+). As the photocatalyst efficiently absorbs photons and adsorbs reactants, these photogenerated e^- and h^+ can participate in redox reactions, reducing and oxidizing pollutants adsorbed on the photocatalyst's surface [3], [4].

Notably, Materials such as modified layered double hydroxides or LDH-based materials have shown potential as photocatalysts [5], [6] in applications such as dye removal from water [7], [8]. LDH are a class of anionic with the formula $[M^{2+}{}_{1-x}M^{3+}{}_x(OH)_2]_\chi^+(A^{n-})_{\chi/n}\cdot mH_2O$, and they are versatile materials with wide range of applications linked to their highly tunable properties. They can incorporate various metallic cations (e.g., Mg^{2+}, Zn^{2+}, Ce^{3+}, Al^{3+}, Fe^{3+}, or Ti^{4+}) [9], enabling tailored bandgap and redox properties for applications like pollutant degradation or dye removal. Their hydroxyl-rich surfaces provide active sites for reactant adsorption and hydroxyl radical formation, enhancing photocatalytic efficiency [7], [10].

While naturally hydrophilic, LDHs can be modified with organic compounds (e.g., dodecyl sulfate or organosilanes) via anion exchange or surface grafting to create hydrophobic surfaces, improving selectivity for non-polar substrates [11]. However, hydrophobicity is not inherent and requires deliberate modification. LDH flexibility in cation composition and surface chemistry makes them promising platforms [9-11].

Lately, the increased interest in photocatalytic films have led to a significant interest in measurements method capable of assessing their effectiveness, one of the well-known methods is the decomposition of stearic acid, which is applied on the surfaces and simulates the organic matter that tend to deposit on the walls [12].

However this method is slow and require dedicated laboratory equipment, thus quicker and easier methods to evaluate the photocatalytic activity of coatings have been developed, and they involve the decomposition of organic dyes, the most popular being methylene blue (MB) where the catalytic performance can be correlated with the change in color or by UV-VIS spectroscopy [13], [14].

Since silver-modified LDH materials such as silver-decorated ZnAl-layered double hydroxide show potential as bacteriostatic materials and theoretically such materials present potential as photocatalysts, in our current work, we studied the photocatalytic properties of a silver modified ZnAl layered double hydroxide applied on mortar surface in the decomposition of methylene blue dye.

2. EXPERIMENTAL PART

The LDH material used was prepared by a coprecipitation technique adapted from [15] starting from the metallic nitrate salts and NaOH + Na_2CO_3 as a precipitating agent. The two solutions were added to a beaker drop by drop while the pH was maintained close to a value of 9-10. The precipitate obtained was aged overnight at 80 °C, cooled to room temperature than filtered and dried in an oven for 8 hours at 80 °C. Its physical-chemical properties were evaluated by X-ray diffraction on powder and X-RAY fluorescence. In order to be applied on the stone surface, the LDH material was grounded in a fine powder, dispersed in distilled water (1g/L) and sonicated in order to finely disperse the particles.

Kinetic stability of the consolidant dispersion in water was measured by performing a turbidimetric analysis with an UV-VIS spectrophotometer (T60, PG Instruments Ltd., Lutterworth, UK). The change in absorbance was measured in time, over a 300 minutes interval (λ = 630 nm at 25 °C) using glass cuvettes with 1 cm optical path. The kinetic stability was calculated using formula (1) [16].

$$KS\% = 1 - \left[\frac{A_0 - A_t}{A_0}\right] \times 100 \quad (1)$$

Powder X-ray diffraction (XRD) for the prepared LDH materials was recorded using a Rigaku X-ray diffractometer with Cu-Ka radiation wavelength equal to 0.15406 nm, operating at 40 kV and 30 mA. The measurements were recorded in the angular range 5–80 2theta at a scan rate of 2° min^{-1}

In order to verify the chemical composition of the prepared materials, wavelength dispersive X-ray fluorescence spectroscopy (WDXRF) was used, with a Rigaku ZSX Primus II spectrometer equipped with an X-ray tube with Rh anode, power 4.0 kW, with front window Be (30 m thick). With the samples being pelleted under vacuum

The substrate chosen was mortar bricks made with quartz sand: gypsum: water of 3:1:0.75 (weight ratio).

To evaluate the photocatalytic activity of silver-modified layered double hydroxide (LDH), we prepared various formulations as outlined in Table 1. For each formulation, two sets of specimens were created: one set was exposed to natural light (I = 700 W/m²) for durations ranging from 65 to 200 hours, while the other set was kept in the dark. Methylene blue degradation was assessed by monitoring the evolution of CIELAB parameters (L*, a*, b*) over time.

Colorimetric analysis using a Konica Minolta colorimeter, Croma-meter CR-410. Ten measurements were performed for each sample, with D65 illuminant and a 2° observer angle.

Solar irradiance was measured in lux using an Extech EasyView 33 light meter and converted to W/m² using a conversion factor of 136 lux per W/m² for natural sunlight, yielding an average irradiance of 700 W/m².

To improve coating adhesion and simulate realistic protective treatments used in heritage conservation, selected specimens were coated with an acrylic primer.

The acrylic layer acted as a binder reducing powder detachment during exposure. The inclusion of both coated and uncoated specimens enabled comparative evaluation of the photocatalytic efficiency and the effect of the acrylic medium on dye degradation under natural light exposure.

Table 1: experimental set-ups

	first substrate	second substrate	third substrate
1	*blanc*	/	/
2	*LDH dispersion*	/	/
3	*MB*	/	/
4	*acryl primer*	/	/
5	*LDH dispersion*	*acryl primer*	/
6	*MB*	*acryl primer*	/
7	*LDH dispersion*	*MB*	*acryl primer*
8	*MB*	*LDH dispersion*	*acryl primer*

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of the Ag@ZnAl-LDH sample. The well-defined diffraction peaks at 2θ = 11.6°, 23.4°, 33.8°, 34.6°, 37.3°, 39.2°, 46.9°, 60.2°, and 61.4° can be indexed to the (003), (006), (101), (012), (104), (015), (018), (110), and (113) planes, respectively, which are characteristic of the ZnAl-LDH structure (JCPDS No. 48-1022) containing carbonate as the interlayer anion [5], [17]. In addition, the reflections at 2θ = 10.3° and 20.6° can also be attributed to the (003) and (006) planes of the LDH structure but suggest the presence of

another compensating anion, likely nitrate (NO_3^-). The extra diffraction lines observed in the pattern correspond to ZnO in the wurtzite phase (JCPDS No. 99-0111) [18], along with several weak reflections attributed to various silver-containing species.

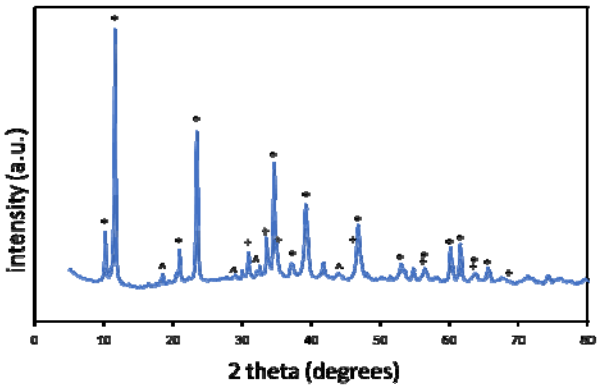

Figure 1. X-ray diffractogram of the LDH material

The crystallite size was calculated according to Debye-Scherrer equation (2) on the stacking direction using the diffraction lines characteristic to (003) planes.

$$D \approx 1.08\lambda / ((2\theta)_{FWHM} * \cos\theta) \quad (2)$$

Where λ is the wavelength of the Cu-Ka radiation and is equal to 0.15406 nm.
The cell parameters, particle size and chemical composition determined by X-ray fluorescence spectroscopy are exhibited in table 2.

Table 2. Cell parameters, crystallite size and chemical composition of the prepared LDH

D (nm)	cell parameters (Å)		chemical composition wt.%			Molar ratios	
	a	c	Al	Zn	Ag	Zn/Al	Ag/M
29.2	3.071	22.63	10.6734	57.3517	7.5099	2.23	0.051

The kinetic stability of the material dispersion shows (figure 3) relatively good values of more than 50 % after 300 minutes, this shows a good stability and a good dispersability in distilled water even at the relatively high values of crystallite sizes

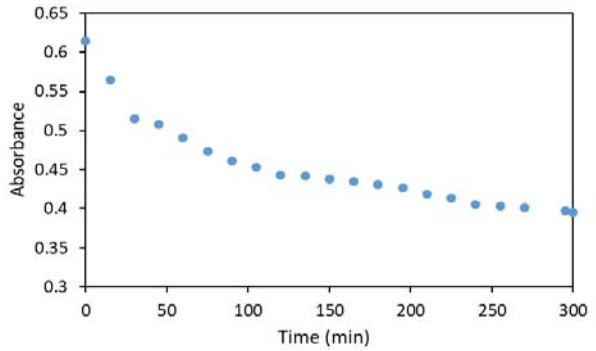

Figure 2. Kinetic stability of Ag-ZnAl-LDH dispersed in distilled water

The visual evaluation of the samples can be seen in figure 3, as expected, the samples kept in the dark shown minuscule change in color with changes in total chromatic parameters DE<0.5 showing that no considerable changes occur in the absence of light.

Additionally, the irradiated samples without methylene blue showed also minute changes in chromatic parameters, showing that applying the LDH dispersion and primer will not modify the surface aestetic parameters or suffer considerable transformation under solar radiation, The total changes in chromatic parameters (L,a.b) are shown in table 3. The "Total change" (ΔL, Δa, Δb) represents the difference between the initial and 200-hour values, indicating the extent of color change, which correlates with MB decomposition.

A larger absolute change in these parameters suggests greater decomposition of MB.
Initial values of parameters a (negative value – green) and b (negative value – blue) shows that the initial samples posseses a greenish - blueish colour that as observed in figure 3 fades after irradiation with varying degrees depending on their composition.

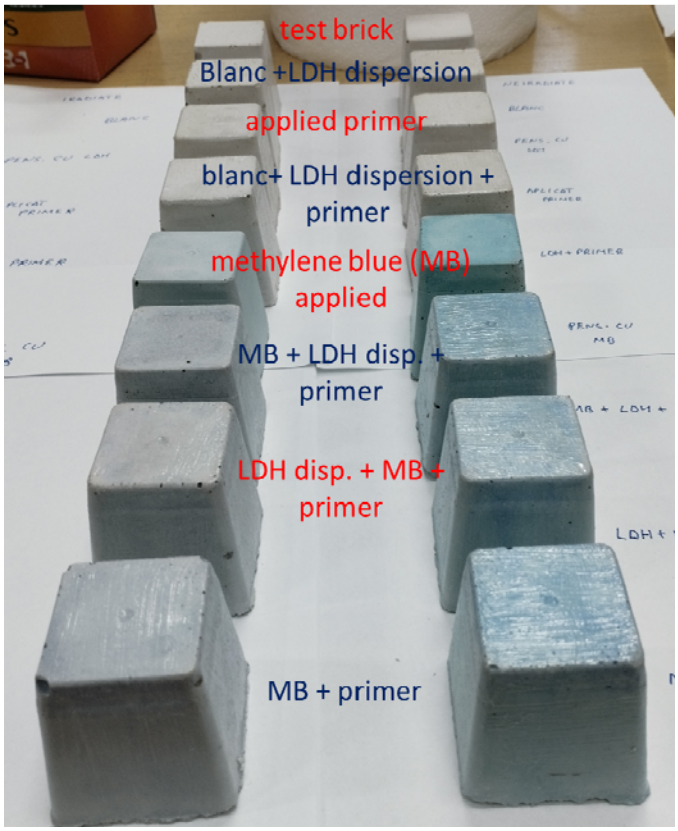

Figure 3. Irradiated specimens vs specimens kept in dark, visual evaluation

Table 3. Chromatic parameters in the samples after various exposure to solar radiation

Sample	Parameter	Time				Total change	
		initial	60 h	160 h	200 h		
MB	L	74.16	76.2075	76.8625	76.9075	-2.7475	ΔL
	a	-8.55	-7.2675	-6.0175	-5.435	-3.115	Δa
	b	-4.89	-3.5625	-2.66	-2.3275	-2.5625	Δb
MB+LDH disp+primer	L	72.1125	73.5025	74.0525	74.32	-2.2075	ΔL
	a	-5.5525	-3.7375	-2.83	-2.51	-3.0425	Δa
	b	-6.3625	-4.5075	-3.16	-2.57	-3.7925	Δb
LDH disp.+MB+primer	L	73.3175	73.3675	74.16	74.3625	-1.045	ΔL
	a	-5.4675	-3.63	-2.73	-2.3825	-3.085	Δa
	b	-4.235	-3.545	-2.1175	-1.64	-2.595	Δb
MB+primer	L	73.3725	74.4675	74.9925	75.375	-2.0025	ΔL
	a	-6.68	-4.6575	-3.515	-3.09	-3.59	Δa
	b	-5.5525	-4.93	-3.6825	-3.2025	-2.35	Δb

Considering Pseudo-First-Order Kinetics: Photocatalytic degradation of dyes like MB typically follows the Langmuir-Hinshelwood model, simplified to pseudo-first-order kinetics at low concentrations [14], [19]:

$$\ln(C_0/C)=kt \quad (3)$$

Where:

C_0 is the initial MB concentration (proportional to initial b or $\Delta E = 0$).
(C) is the MB concentration at time t (proportional to b).
(k) is the rate constant (h^{-1}).
(t) is the irradiation time (hours).

Since direct concentration data isn't available, we'll assume that the b parameter (or ΔE) is linearly related to MB concentration. Thus, we'll use the value of b parameter instead of concentration to obtain the the apparent first-order rate constant table 4.
As shown in table 4, it is thus clear that the application of Ag-ZnAl-LDH dispersion improve the rate of methylene blue degradation both when used before the dye and when used on stained surface

The rate constant however is lower for solid surfaces compared to a liquid environment where the molecules have additional degrees of liberty [14]. While given the condition at the brick surface (pH neutral or slightly basic) we can assume that the photocatalytic MB degradation takes place via interaction with oxygen vacancy (MB+h+→ mineralized product) [20]. This is in line with the known electronic properties of ZnAl-LDH that are also promoted by the presence of ZnO and poorly crystallized silver containing phases also present on the ZnAl-LDH sheets, silver particle known to stabilize the hole-electron pairs [5].

Table 4. Rate constant for methylene blue degradation based on b parameter from CIELAB measurements

Sample	Rate Constant (k, h^{-1})	R^2 (Fit Quality)
MB	0.0037	0.98
MB + LDH disp.+ primer	0.0045	0.99
LDH disp. + MB + primer	0.0047	0.92
MB + primer	0.0027	0.99

4. CONCLUSIONS

This study investigated the photocatalytic performance of silver-modified ZnAl-layered double hydroxide (Ag@ZnAl-LDH) coatings applied on mortar surfaces for the degradation of methylene blue (MB) under natural light exposure. The following conclusions can be drawn:

The Ag@ZnAl-LDH was successfully synthesized via a coprecipitation method, exhibiting characteristic diffraction lines for LDH structure (JCPDS No. 48-1022) with carbonate and nitrate as interlayer anions, alongside minor ZnO and silver-containing phases. The material demonstrated a crystallite size of 29.2 nm, good kinetic stability in aqueous dispersion (>50% after 300 minutes), and a chemical composition very close to the intended values.

The degradation of MB follows pseudo-first-order kinetics, with rate constants ranging from 0.0027 h^{-1} (MB + primer) to 0.0047 h^{-1} (LDH disp. + MB + primer). The higher rate constants for LDH-containing samples indicate that Ag@ZnAl-LDH enhances photocatalytic efficiency, likely due to the synergistic effects of ZnO and silver-containing phases stabilizing electron-hole pairs and facilitating redox reactions via oxygen vacancies. It is also noteworthy that the use of the primer although usefull to stabilize the surface, seem to inhibit the decomposition of methylene blue in the absence of catalyst.

The Ag@ZnAl-LDH coating demonstrates promise as a multifunctional protective treatment for stone-based heritage structures especially porous stone. Its photocatalytic activity effectively enhances the decomposition of degrades organic dyes such as MB, while its bacteriostatic potential (owing to silver modification) and stability in aqueous dispersions make it a versatile candidate for preserving both the structural integrity and aesthetic appeal of cultural monuments in urban environments.

Further development is necessary for obtaining more effective photocatalytic materials.

ACKNOWLEDGEMENTS:

This work received financial support from the project PN 23.06 NUCLEU Program-ChemNewDeal within the National Plan for Research, Development and Innovation 2022–2027, developed with the support of Ministry of Education and Research – National Research Authority, project no. PN 23.06.02.01 (InteGral).

REFERENCES

[1] C. Esposito Corcione, C. Ingrosso, F. Petronella, R. Comparelli, M. Striccoli, A. Agostiano, M. Frigione, M.L. Curri, A designed UV–vis light curable coating nanocomposite based on colloidal TiO2 NRs in a hybrid resin for stone protection, Prog. Org. Coatings. 122 (2018) 290–301. https://doi.org/10.1016/j.porgcoat.2018.05.020.

[2] L. Graziani, E. Quagliarini, A. Osimani, L. Aquilanti, F. Clementi, C. Yéprémian, V. Lariccia, S. Amoroso, M. D'Orazio, Evaluation of inhibitory effect of TiO2 nanocoatings against microalgal growth on clay brick façades under weak UV exposure conditions, Build. Environ. 64 (2013) 38–45. https://doi.org/10.1016/j.buildenv.2013.03.003.

[3] J.M. Herrmann, C. Duchamp, M. Karkmaz, B.T. Hoai, H. Lachheb, E. Puzenat, C. Guillard, Environmental green chemistry as defined by photocatalysis, J. Hazard. Mater. 146 (2007) 624–629. https://doi.org/10.1016/j.jhazmat.2007.04.095.

[4] M.A. Ali, I.M. Maafa, Recent literature review of Cerium-containing photocatalysts used for methylene blue degradation, J. Hazard. Mater. Adv. 16 (2024) 100486. https://doi.org/10.1016/j.hazadv.2024.100486.

[5] J.C. Shen, H.Y. Zeng, C.R. Chen, S. Xu, A facile fabrication of Ag2O-Ag/ZnAl-oxides with enhanced visible-light photocatalytic performance for tetracycline degradation, Appl. Clay Sci. 185 (2020) 105413. https://doi.org/10.1016/j.clay.2019.105413.

[6] M. Hadnadjev-Kostic, T. Vulic, R. Marinkovic-Neducin, D. Lončarević, J. Dostanić, S. Markov, D. Jovanović, Photo-induced properties of photocatalysts: A study on the modified structural, optical and textural properties of TiO2–ZnAl layered double hydroxide based materials, J. Clean. Prod. 164 (2017) 1–18. https://doi.org/10.1016/j.jclepro.2017.06.091.

[7] S. Nayak, K. Kumar Das, K. Parida, Indulgent of the physiochemical features of MgCr-LDH nanosheets towards photodegradation process of methylene blue, J. Colloid Interface Sci. 634 (2023) 121–137. https://doi.org/10.1016/j.jcis.2022.12.050.

[8] E.M. Seftel, M. Niarchos, C. Mitropoulos, M. Mertens, E.F. Vansant, P. Cool, Photocatalytic removal of phenol and methylene-blue in aqueous media using TiO2@LDH clay nanocomposites, Catal. Today. 252 (2015) 120–127. https://doi.org/10.1016/j.cattod.2014.10.030.

[9] F. Cavani, F. Trifirò, A. Vaccari, Hydrotalcite-type anionic clays: Preparation, properties and applications., Catal. Today. 11 (1991) 173–301. https://doi.org/10.1016/0920-5861(91)80068-K.

[10] H. Fan, J. Zhu, J. Sun, S. Zhang, S. Ai, Ag/AgBr/Co-Ni-NO3 layered double hydroxide nanocomposites with highly adsorptive and photocatalytic properties, Chem. - A Eur. J. 19 (2013) 2523–2530. https://doi.org/10.1002/chem.201203408.

[11] R. He, S. Liu, R. Wang, T. Fu, R. Zhang, Q. Zhang, Y. Zhou, In situ modification of melamine sponge by MgAl-LDH with super-hydrophobicity and excellent harsh environment tolerance for high flux emulsion separation, Sep. Purif. Technol. 291 (2022) 120916. https://doi.org/10.1016/j.seppur.2022.120916.

[12] A. Mills, M. McFarlane, Current and possible future methods of assessing the activities of photocatalyst films, Catal. Today. 129 (2007) 22–28. https://doi.org/10.1016/j.cattod.2007.06.046.

[13] R.S. Sonawane, S.G. Hegde, M.K. Dongare, Preparation of titanium(IV) oxide thin film photocatalyst by sol–gel dip coating, Mater. Chem. Phys. 77 (2002) 744–750.

[14] E.A. El-Sharkawy, A.Y. Soliman, K.M. Al-Amer, Comparative study for the removal of methylene blue via adsorption and photocatalytic degradation, J. Colloid Interface Sci. 310 (2007) 498–508. https://doi.org/10.1016/j.jcis.2007.02.013.

[15] T.T.T. Le Hoang, N. Insin, N. Sukpirom, Catalytic activity of silver nanoparticles anchored on layered double hydroxides and hydroxyapatite, Inorg. Chem. Commun. 121 (2020) 108199. https://doi.org/10.1016/j.inoche.2020.108199.

[16] G. Taglieri, J. Otero, V. Daniele, G. Gioia, L. Macera, V. Starinieri, A.E. Charola, The biocalcarenite stone of Agrigento (Italy): Preliminary investigations of compatible nanolime treatments, J. Cult. Herit. 30 (2018) 92–99. https://doi.org/10.1016/j.culher.2017.11.003.

[17] Y. Yang, L. Yan, J. Li, J. Li, T. Yan, M. Sun, Z. Pei, Synergistic adsorption and photocatalytic reduction of Cr(VI) using Zn-Al-layered double hydroxide and TiO2 composites, Appl. Surf. Sci. 492 (2019) 487–496. https://doi.org/10.1016/j.apsusc.2019.06.229.

[18] C.M. Chou, Y.C. Chang, P.S. Lin, F.K. Liu, Growth of Cu-doped ZnO nanowires or ZnO-CuO nanowires on the same brass foil with high performance photocatalytic activity and stability, Mater. Chem. Phys. 201 (2017) 18–25. https://doi.org/10.1016/j.matchemphys.2017.08.023.

[19] M.I. Din, R. Khalid, J. Najeeb, Z. Hussain, Fundamentals and photocatalysis of methylene blue dye using various nanocatalytic assemblies- a critical review, J. Clean. Prod. 298 (2021) 126567. https://doi.org/10.1016/j.jclepro.2021.126567.

[20] J. Zita, J. Krýsa, A. Mills, Correlation of oxidative and reductive dye bleaching on TiO2 photocatalyst films, J. Photochem. Photobiol. A Chem. 203 (2009) 119–124. https://doi.org/10.1016/j.jphotochem.2008.12.029.