Synthesis of layered zinc-aluminium double hydroxides modified with metal ions as photocatalysts with enhanced sorption properties

Olga Długosz1 · Marcin Banach1

Received: 25 May 2022 / Accepted: 7 September 2022 / Published online: 25 September 2022 © The Author(s) 2022

Abstract
In the article the process of Fe, Co, Ni and Cu hydroxides modified nanoparticles of layered double hydroxides (LDH) based on Zn and Al (Zn-Al LDH) was successfully presented. The precipitation method allowed to obtain nanoparticles of high crystallinity with lateral dimensions below 100 nm and thickness below 20 nm. The photocatalytic activity of the modified LDH in the degradation process of quinoline yellow was over 99%, while for the unmodified LDH the efficiency was only 30%. The study confirmed that modification of LDH with divalent ions had a significant effect on both photocatalytic and sorption properties. Furthermore, the study also investigated the effect of the nature of the type of light on the photodegradation efficiency.

Keywords LDH nanoparticles · Metal hydroxides modification · Sorption · Photocatalysis · Ultraviolet · Visible light

1 Introduction
Layered double hydroxides (LDH) are a group of two-dimensional materials generally described by the formula \( [\text{M}^2+_{1-x} \text{M}^3+_{x} (\text{OH})_2]^{(3-x)/2} [\text{A}^{n-}]_{n/x} \cdot m\text{H}_2\text{O} \), where \( \text{M}^2+ \) refers to metal cations e.g. \( \text{Mg}^{2+}, \text{Ca}^{2+}, \text{Co}^{2+}, \text{Zn}^{2+}, \text{Cu}^{2+}, \text{Ni}^{2+}, \text{and} \text{M}^3+ \) indicates the trivalent metal cations, e.g. \( \text{Al}^{3+}, \text{Co}^{3+}, \text{Fe}^{3+}, \text{Cr}^{3+}, \text{Ni}^{3+}, \text{Cu}^{3+} \) [1]. The \( \text{M}^2+ \) and \( \text{M}^3+ \) cations are distributed in the hydroxide layer and \( \text{A}^{n-} \) are anions located in the interlayer space, which can be inorganic \( (\text{O}_2^{2-}, \text{NO}_3^-, \text{Cl}^-) \), organic (e.g. carboxylate, oxoanion) or complex (e.g. coordination compounds or polyoxometalates) [2]. The individual layers of cations in the LDH structure are held together by bonds formed between metal cations and anions in the interlayer space. An example of a naturally occurring LDH is hydrotalcite, which consists of magnesium or aluminium ions (Mg\(^{2+}\) and Al\(^{3+}\)) with carbonate ions CO\(_3^{2-}\) [3].

Due to the possibility of manoeuvring the composition of LDH nanoparticles and the selection of ions, these materials exhibit a wide range of properties and find applications as catalysts, sorbents, photocatalysts, drug carriers, flame retardant materials, additives with antimicrobial properties, etc. [4]. An unquestionable advantage of these materials is their developed specific surface area resulting from the layered structure [5]. Nuzhin et al. have shown that copper- and clay-based LDH catalyses the N-methylation reactions of p-anisidine [2]. The developed surface enabled the initiation of surface reactions increasing the catalytic efficiency of the materials. Layered double hydroxides are also increasingly proposed for biomedical applications [6, 7]. Their biocompatibility, anion-exchange capacity, nanometric particle size, high chemical stability, and the ability to adjust the surface charge of the particles enable controlled release and permeation of active substances without the deleterious effects of LDHs themselves. Furthermore, LDHs presenting hydrophilic character are used as inorganic nanofillers to produce polymeric nanocomposite membranes for water treatment [8].

LDH materials can assist in the treatment of dye wastewaters from the textile, leather, paper, cosmetics, and plastics industries and beyond [9–11]. There are several types of dyes used in industry, most of which are toxic, mutagenic, and carcinogenic. Among the known methods of wastewater treatment, there are physical (evaporation, distillation, sedimentation, adsorption) and chemical methods (chlorination, ozonation), but photocatalysis, being a physico-chemical method, is one of the most promising, as organic pollutants

* Olga Długosz
olga.dlugosz@pk.edu.pl

1 Faculty of Chemical Engineering and Technology, Cracow University of Technology, Warszawska St. 24, 31-155 Cracow, Poland
are converted into non-toxic simple compounds, mainly CO₂
and H₂O [10, 12, 13]. The challenge, however, is to develop
materials that would increase the rate of dye removal. This
effect would be achieved by combining materials with high
photocatalytic activity and good sorption properties. In
recent years, layered double hydroxides and their derivative
structures have gained interest in photocatalytic applications
due to their ability to efficiently sorb pollutants and their
progressive photodegradation under both UV and visible
light.

The aim of this study was to modify the structure of lay-
ered double hydroxides based on zinc and aluminium by
adding divalent hydroxides (Me(OH)₂). The modified mate-
rials differed in structure, surface area and particle size,
which affected their sorption and photocatalytic properties.
In this manner, active materials were obtained, which can be
successfully used to remove a wide range of contaminants
[14, 15].

2 Experimental section

2.1 Materials

The syntheses of layered double hydroxides were carried
out with use of zinc nitrate (V) (Zn(NO₃)₂·H₂O, Sigma-
Aldrich), aluminium nitrate (V) (Al(NO₃)₃·H₂O, Merck),
sodium hydroxide (NaOH, Sigma-Aldrich) and sodium
carbonate (Na₂CO₃, Sigma-Aldrich). The Zn-Al LDH were
modified by introducing selected metal ions into hydroxide
layers. For this reason, iron(II) chloride (FeCl₂·H₂O, Acros),
nickel chloride (NiCl₂·H₂O, Sigma-Aldrich), cobalt(II) chlo-
ride (CoCl₂·H₂O, Sigma-Aldrich), and copper(II) chloride
(CuCl₂, Sigma-Aldrich) were used.

2.2 Methods of LDH nanoparticles synthesis

Process of synthesis of layered double hydroxides (Zn-
Al-LDH) was carried out in batch system. For this reason
10 g Zn(NO₃)₂ and 15 g Al(NO₃)₃ were dissolved in 200
cm³ deionized water. Simultaneously, 5 g NaOH with 4 g
Na₂CO₃ were dissolved in 30 cm³ of water. The solution
of metal ions was heated into 50 °C and 30 cm³ of alkali
dsolution was dropped. The solution was mixed in 200 rpm
by 4 h, filtered, washed, and dried in 50 °C overnight. Syn-
theses of Me-LDH (Fe–Zn–Al LDH, Cu–Zn–Al LDH, Co-
Zn-Al LDH and Ni–Zn–Al LDH) were carried out by adding
selected metal salt into solution of Zn(NO₃)₂ and Al(NO₃)₃.
The molar ratio of Me:Zn was 0.5:1, 0.75:1 and 1:1 (desig-
nation for example Fe0.5-Zn-Al LDH, Fe0.75-Zn-Al LDH
and Fe1-Zn-Al LDH).

2.3 Instrumental analysis

The size of the resulting nanoparticles and LDH crystal-
lites were determined by DLS and XRD analyses (Philips
X’Pert camera with monochromator PW 1752/00 CuKα),
respectively. The phase composition was described using
the Rietveld method based on Match! program. The XRD
analysis, combined with Scherrer equation for crystallite
size, enabled the determination of actual LDH crystallite
sizes. Differences in morphology of the obtained prod-
ucts were observed based on SEM microphotographs. The
SEM–EDS analysis allowed determining the distribution
of individual elements in LDH structures. Impact of addi-
tion of the metals on band gaps of the LDH material was
established based on UV–Vis spectrophotometer Rayleigh
1800. The materials were also compared in terms of the
surface character of the materials obtained. In this pur-
pose, the point of zero charge was established in the Zeta
Sizer Malvern. Based on the DLS method, the hydroun-
dynamic diameter of LDH particles suspended in water was
also determined. The presence of the special groups in
the materials, including the occurrence of –CO₃, –OH,
–NO₃, etc., was confirmed by FTIR. Active surface area
of LDH nanoparticles and pore volume were measured
on a Gemini VI apparatus from Micromeritics USA. The
qualitative composition of the materials was determined
by XPS X-ray Photoelectron Spectroscopy analysis. The
analyses were carried out on a PHI Quantum 2000, Physical
Electronics, Inc.: Photoelectron excitation source: a
VG Scienta SAX 100 X-ray tube with an aluminium anode,
equipped with a VG Scienta XM 780 monochromator,
emitting radiation with an Al Kα characteristic line and
an energy of 1486.7 eV.

2.4 Photocatalytic studies

2.4.1 Photodegradation properties of Zn-Al LDH

Photocatalytic properties of Zn-Al LDH nanoparticles were
determined during photodegradation of quinoline yellow
(Sigma-Aldrich). In each process, 50 mg of the material
was mixed with 200 cm³ of 100 mg/dm³ solution of the dye.
After 30 min in the darkness, samples were mixed in the
presence of UV light (365 nm) for 60 min. The effectiveness
of photodegradation was calculated based on the equation:

\[
E = \frac{C_0 - C_t}{C_0} \times 100\
\]

where \(C_0\) is an initial concentration of the dye, \(C_t\) is a con-
centration of the dye after t min of the photodegradation.
The absorbance of the degraded dye was measured by UV–Vis spectroscopy (Rayleigh UV-1800 spectrophotometer).

2.4.2 Cycle efficiency of materials

The stability of the materials and their photocatalytic activity was investigated in cyclic processes. After photodegradation, each material was washed, filtered, and dried. In each catalytic step 200 mg of the material was mixed with new 200 cm$^3$ of 100 mg/dm$^3$ quinoline yellow solution.

2.4.3 Scavenging experiments for reactive species

To characterise the mechanism of photocatalysis on LDH nanoparticles, photodegradation processes were carried out in the presence of selected scavengers: triethanolamine (TEOA (H$^+$), $C_0=1$ mmol/dm$^3$), benzoquinone (BQ (O$_2^-$), $C_0=0.5$ mmol/dm$^3$) and mannitol ((-OH), $C_0=1$ mmol/dm$^3$) and silver nitrate(V) (AgNO$_3$ (e$^-$), $C_0=1$ mmol/dm$^3$). For this purpose, 50 mg of material was added to 20 cm$^3$ of solution in which the dye concentration was 100 mg/dm$^3$ and the scavenger concentration was 1 or 0.5 mmol/dm$^3$, respectively. After 30 min of running the process in the dark, the suspensions were stirred for 60 min in the presence of UV light (365 nm). The solutions were then filtered and the filtrate was analysed in terms of quinoline yellow concentration. The addition of selected compounds: triethanolamine, benzoquinone, mannitol, and silver nitrate(V) allowed the determination of which radicals are involved in the photodegradation process. Based on the results it was possible to investigate the mechanism of photodegradation on LDH photocatalysts.

3 Results

3.1 Selection of Me$^{2+}$ modification for LDH of nanoparticles

3.1.1 Effect of Me$^{2+}$ modification on LDH structure

Zn-Al LDH nanoparticles with addition of Fe, Cu, Ni, and Co hydroxides with molar ratio of Me to Zn equal to 0.5, 0.75, and 1.0 were prepared in batch processes. The composition of materials is shown in Table 1. The obtained materials were examined to select the materials with the highest photocatalytic activity.

All diffractograms confirmed the presence of six diffraction peaks characteristic of LDH structures, at 11.6° (003), 23.3° (006), 34.5° (102), 39.12° (105), 46.6° (108), and 60.1° (110) [16]. No other phases indicative of impurities were observed. Characteristic peaks confirming LDH formation are those indexed as 003 and 006, appearing as strong/sharp, narrow, and symmetrical diffraction peaks (Fig. 1). These peaks determine the basal reflections of intercalated NO$_3^-$, CO$_3^{2-}$ anions located in the LDH interplane space, with the first basal reflection (003) appearing with greater intensity than the second basal reflection (006), as confirmed by literature sources [17, 18]. Materials without the addition of Me hydroxides showed higher crystallinity than materials with the addition of Fe, Cu, Co, and Ni hydroxides. These differences can be explained by an enhanced randomness in the formation of layers which included cations of different sizes [16].

Based on crystallographic analysis, the nanoparticles were revealed to be hexagonal in nature, corresponding to an $R-3m$ structure (166) [19]. LDH nanoparticles were analysed to determine the basal distances and crystallite sizes of

| LDH material          | Theoretical molar ratio of Me to Zn | Basal spacing \(d_{\text{B}}\) [nm] | \(H_{\text{LDH}}\) [Å] | \(a\) [Å] | \(c\) [Å] |
|-----------------------|-------------------------------------|-------------------------------------|-------------------------|----------|---------|
| Zn-Al LDH             | 0.00                                | 0.7607                              | 23.40                   | 1.00     | 3.0424  | 22.6641 |
| Fe0.5-Zn-Al LDH       | 0.50                                | 0.7558                              | 24.32                   | 0.59     | 3.0763  | 22.6599 |
| Fe0.75-Zn-Al LDH      | 0.75                                | 0.7503                              | 22.58                   | 0.33     | 3.0648  | 22.5125 |
| Fe1.0-Zn-Al LDH       | 1.00                                | 0.7540                              | 17.08                   | 0.18     | 3.0484  | 22.4517 |
| Ni0.5-Zn-Al LDH       | 0.50                                | 0.7625                              | 14.04                   | 0.42     | 3.0710  | 22.8562 |
| Ni0.75-Zn-Al LDH      | 0.75                                | 0.7608                              | 10.98                   | 0.37     | 3.0670  | 22.9049 |
| Ni1.0-Zn-Al LDH       | 1.00                                | 0.7647                              | 9.40                    | 0.28     | 3.0556  | 22.9035 |
| Cu0.5-Zn-Al LDH       | 0.50                                | 0.7666                              | 18.15                   | 0.66     | 3.0762  | 22.8071 |
| Cu0.75-Zn-Al LDH      | 0.75                                | 0.7615                              | 22.34                   | 0.71     | 3.0765  | 22.8184 |
| Cu1.0-Zn-Al LDH       | 1.00                                | 0.7602                              | 26.91                   | 0.83     | 3.0708  | 22.7590 |
| Co0.5-Zn-Al LDH       | 0.50                                | 0.7619                              | 21.72                   | 0.46     | 3.0762  | 22.8354 |
| Co0.75-Zn-Al LDH      | 0.75                                | 0.7586                              | 20.18                   | 0.37     | 3.0787  | 22.8957 |
| Co1.0-Zn-Al LDH       | 1.00                                | 0.7681                              | 23.95                   | 0.34     | 3.0858  | 23.0352 |
the nanoparticles. Basal distance is defined as the distance from the plane of the layer to the adjacent layer. The basal distance and crystal size data corresponding to the individual characterization peaks are given in Table 1. The lattice parameters of LDH with Me(OH)$_2$ addition assume slightly larger basal space values ($d(003)$) compared to basal LDH, the exception being the addition of Fe(OH)$_2$. This may be due to the smaller ionic radius of Fe$^{2+}$ (63 pm) compared to the ionic radii of Zn$^{2+}$ (74.5 pm), Ni$^{2+}$ (70 pm), Cu$^{2+}$ (73 pm) and Co$^{2+}$ (73.5 pm) [20]. The cell parameter $a$, which represents the distance between cations within the LDH layer ($a = 2d(110)$), remains approximately constant (Table 1). The parameter $c$, whose adhesion distance to the hydroxide layer is given by $c = 3d(003)$, where $d = \lambda/2 \sin \theta$, varies with the added Me(OH)$_2$. This behaviour is related to the presence of oxygen-containing functional groups in the growth of LDH crystallites.

The preparation of LDH by changing the metal ion ratio can result in variation in nanostructure growth rates and network parameters of the materials (Table 1). An increase in the proportion of Me(OH)$_2$ in the LDH structure resulted in a decrease in LDH crystallinity, with the greatest differences observed for materials with Ni$^{2+}$ or Fe$^{2+}$. Kulkarni et al. revealed variations in the platelet size of the obtained Ni–Co LDHs (Ni:Co ratio = 1:0, 0.75:0.25, 0.5:0.5, 0.4:0.6, 0.25:0.75, and 0:1), as well as the occurrence of differences in the pore size and number of layers of the materials depending on the proportion of each ion. The authors noted that the amount of nickel in the layer is a determining factor in LDH morphology. Changing the molar ratio of Ni–Co metal ions of 0, 0.3, 0.6, 1, 3, and 1 revealed a reduction in the crystallinity of the materials, in which a reduction in the content of accessory metal ions leads to sharp and intense peaks of the hydrotalcite phase, showing good crystallinity of the LDHs [21]. It is suggested that increasing the molar ratio of additional hydroxide to Zn(OH)$_2$ increases the amorphous character of LDH. Concurrently, the use of various metals with different ionic radii, affect the rate of hydroxide crystal formation and deform the layered structure of LDH.

### 3.2 Effect of Me(OH)$_2$ addition on photocatalytic properties of Zn–Al LDH

Table 2 shows the efficiency of LDH nanoparticles in quinoline yellow (QY) photodegradation process, depending on its concentration in the product. Based on the results, it was found that the highest photodegradation efficiency of QY is obtained for the materials with 0.5 addition in relation to the number of moles of Zn$^{2+}$. In parallel, among the added metal ions, the highest efficiency was obtained for Ni0.5-Zn–Al LDH. As mentioned, the content of metal ions above 0.5 mol in relation to Zn$^{2+}$ ions cause a decrease in crystallinity of materials and modification of their structure, which results in deterioration their photocatalytic properties. However, a
positive correlation was observed between the presence of Me(OH)₂ and the improvement of photocatalytic properties. Due to the developed LDH surface area, a significant contribution of dye sorption was observed, which influences at a further stage the surface processes allowing the degradation of the dye structure to simpler forms. It is suggested that the addition of Me hydroxide may have limited effect of reducing the energy gap width of LDH but enhancing the sorption efficiency of the materials by disrupting their structure. On this basis, LDH nanoparticles with addition of Ni(OH)₂ with a molar ratio of Ni:Zn equals to 0.5:1:0 were selected for subsequent studies.

Similar results related to the change in intensity of diffraction peaks with increasing Ni(OH)₂ content were confirmed by Paikaray et al. The authors suggested that nickel ions build into the structure of the forming LDH particles, as noted by the decreasing parameter a. An increase in Ni(OH)₂ content decreases the distances between cations, which is due to the replacement of Zn²⁺ ions with Ni²⁺ ions in the crystal structure. Similarly, as described by the authors in their study, higher values of parameter c were obtained in Ni–Zn–Al LDH materials, indicating an expansion of the interlayer spacing. The reported results, combined with the decreasing size of the crystallites, confirm the growth of disorder in the LDH structure [22]. Compared with literature data, it was confirmed that LDH crystals become less amorphous with the increase in their size running in parallel with the nucleation process [23, 24].

### 3.3 Characterization of Zn–Al LDH and Ni–Zn–Al LDH nanoparticles

#### 3.3.1 Analysis of SEM and SEM–EDS LDH nanoparticles

SEM microphotographs of the obtained LDH nanoparticles are shown in Figs. 2 and 3. Nanoplates with diameters of about 100–272 nm and thicknesses ranging from 13.5–36.0 nm were obtained, depending on the method used. SEM–EDS analysis confirmed a uniform distribution of Zn, Ni, Al, O, and C (Fig. 2.II). Ma et al. obtained γ-Fe₂O₃/NiO with a thickness of about 100–272 nm and an approximate thickness of 5–50 nm [25]. The addition of nickel (Fig. 2.B) further influences the reduction in size of LDH nanoparticles regardless of the modification of the method.

#### 3.3.2 Particle size analysis by DLS and the point of zero charge analysis

Table 3 shows the particle sizes of the obtained LDH materials and the point of zero charge (PZC) values. The addition of nickel hydroxide resulted in nanoparticles with smaller sizes for LDH materials. The surface charge of the materials was investigated by analysing the results with the photodegradation efficiency of QY and MB, which, with similar molecular weight, differ in ionic character. The determined PZC values were 7.99 for Zn–Al LDH and 7.05 for NiO.5–Zn–Al LDH. The value of the point of zero charge for nickel-modified LDH materials resulted in a shift of the charge value towards neutral. The shift of the surface character from negative to neutral facilitates the sorption of negatively charged materials, which increases the applicability of the material, being more versatile for a wide range of compounds.

The energy band gap values equalled 3.29 eV for both Zn–Al LDH and NiO.5–Zn–Al LDH. These values were comparable to those obtained for ZnO [26]. Despite the increased energy gap of nickel, there was no increase in the BG of modified LDH. This confirms that the presence of nickel hydroxide in the structure favourably increases the active surface area of the photocatalyst, without a decrease in the energy band gap value, which would require the use of high-energy radiation, preventing the catalyst from being active under visible light as well.

#### 3.3.3 The BET analysis

The active surface area of Zn–Al LDH and nickel hydroxide-modified LDH nanoparticles (NiO.5–Zn–Al LDH) was determined by BET analysis (Table 4.) The active surface area more than doubles after nickel addition to the LDH structure. Zn–Al LDH consists mainly of nanopores with diameters below 1 nm and a small proportion of micropores with sizes of 5–50 nm (Fig. 4). The P/P₀ plot takes the form of type II hysteresis, which corresponds to the formation of pores between the two planes associated with the plane structure of LDH nanoparticles [27]. The addition of nickel hydroxide changes the shape of the hysteresis, indicating an increase in the interplane space. This change correlates with an increase in the active surface area of the NiO.5–Zn–Al LDH material, compared to Zn-Al LDH. In addition to micropores, the presence of mesopores with a
size of 5–30 nm is also observed, so that the pore volume is increased by four times compared to Zn-Al LDH [28].

3.4 FTIR analysis of LDH nanoparticles

The type and structure of ions forming the Zn–Al LDH and Ni0.5–Zn–Al LDH layers were investigated by FTIR spectroscopy (Fig. 5). The broad absorption band with a maximum at 3422 cm\(^{-1}\) comes from –OH stretching vibrations. Due to the absence of a band at about 1600 cm\(^{-1}\), it is suggested that the –OH bonds correspond to the hydroxide groups of LDH structures [27]. The high-intensity absorption peaks at 1360 and 779 cm\(^{-1}\) derive from symmetric stretching vibrations and out-of-plane deformation vibrations of CO\(_3^{2-}\) ions, indicating the presence of interstitial carbonate ions [8]. The higher band intensity at 1360 cm\(^{-1}\) suggests an ordered arrangement of CO\(_3^{2-}\) ions between layers of LDH nanoparticles. The weak absorptions in the low-frequency region of 550 and 460 cm\(^{-1}\) are attributed to the stretching bonds of –MeO and bending bonds of MeOH octahedral hydroxyl sheets [25]. Absorption peaks in the 800–650 cm\(^{-1}\) range are associated with vibrations of the Me–O–Me and O–Me–O bonds [29].

After the quinoline yellow photodegradation process, the materials were studied again by FTIR analysis. No significant differences were observed between the spectra, indicating the absence of structural changes in the materials. The lack of differences between the spectra also confirms the photocatalysis process, by which the dye molecules are degraded. If only the process of sorption of the dye had taken place, it would have been possible to observe additional bands corresponding to the C=C, C–C, C–H bonds, among others, forming the dye molecules [27].

3.4.1 The XPS analysis

In order to better understand the composition of the LDH nanoparticles as well as the existing functional groups that build up the LDH layers, XPS analysis was performed. The broad spectrum (Fig. 6) confirmed the presence of Zn, Al, Ni, C, O, Cl. Figure 5 shows the deconvolution of the main peaks (Ni-2p, Al-2p, Zn-2p, C-1 s, and O-1 s) of the high-resolution XPS spectrum. Table 5 shows the quantitative composition of the LDH materials and in which functional groups the elements occur. Ni-2p, Zn-2p, and Al-2p indicate
that the oxidation state of these elements is mainly based on ions [30].

The results show that the valence state of zinc on the Ni0.5–Zn–Al LDH surface is +2 (Lu et al. 2017). The high-resolution Zn-2p spectrum showed three deconvoluted peaks located at 1021.91, 1022.62, and 1023.74 eV, which were assigned to Zn–OH, Zn–CO₃, and in a small proportion of Zn–Cl, respectively [11]. The O1s spectrum displays signals from all oxygen species on the surface. The oxygen peak at 531.15 eV corresponds to a mixture of oxygen from the Ni0.5–Zn–Al LDH structure. XPS analysis shows that Ni²⁺ and Al³⁺ elements coexist in the product, which is in agreement with predictions [31]. Analysis confirmed the formation of Ni(OH)₂, Zn(OH)₂, and Al(OH)₃ [32]. The formation of additional forms of metal carbonates, mainly ZnCO₃, was also confirmed.
3.5 The photocatalytic properties of LDH nanoparticles

3.5.1 Photodegradation of quinoline yellow QY under UV and visible light

To determine the photocatalytic activity of the obtained LDH, tests were carried out in the presence of various sources of light. Based on previous tests, the influence of the type of light source was investigated on two materials: Zn–Al LDH and Ni0.5–Zn–Al LDH. The reactions were carried out at natural pH (6.8). In the first step, the samples were mixed with the dye solution for 30 min in the darkroom. In the processes, the proportion of sorption was between 40 and 60%, which can be explained by the developed layered structure of the materials, as well as by the good adhesion of neutral QY to the neutral character of the photocatalyst surfaces.

Figure 7 presents the decomposition process of the dye. Graphs presenting the concentration of QY as a function of exposure time showed that regardless of the addition of metal ions, all samples exhibited higher photocatalytic activity compared to the base LDH, but the addition of Ni improved the photodegradation efficiency of QY to the highest extent. The high photocatalytic activity of LDH with Ni addition may be due to the formation of smaller particles and the reduction in the anionic character of the catalyst surfaces [34]. The addition of ions also improves the adhesion of the inert dye to the surface of the materials. It was shown that for Ni0.5–Zn–Al LDH materials irrespective of the method of preparation, the percentage of decolorization was greater than 90%, which corresponds to the removal of 27 mg QY/g of catalyst and is higher than for base LDH (82% corresponds to 24.5 mg/dm$^3$). The process rate constants after LDH modification with Ni are more than 5 times higher, indicating a significant improvement in reaction rates.

3.5.2 Cyclic investigation of LDH nanoparticles

The stability of LDH photocatalysts was investigated in three cycles of QY photodegradation operation. The materials were stable and provided almost constant percentage of photodegradation after three cycles (Fig. 8). Liji confirmed the stable performance of LDH-based materials. The authors found that Au–Pd nanoparticles immobilized on Ni–Fe–CO$_3$ LDH are good photocatalysts degrading about 95% of the dye (25 mg/dm$^3$) after 60 min and the activity remains almost the same after recycling the catalyst [35].

In successive cycles of operation, a decrease in the sorption contribution to the removal of QY was observed, but the rate of photodegradation of the dye remained constant ensuring their effectiveness at longer time of use. In all materials, the slope curve of the dye concentration over time becomes steeper, indicating an increasing contribution of photocatalysis to dye removal and an improvement in the photocatalytic properties of the materials. The results of the high stability performance of LDH nanoparticles were confirmed by Abderrazek et al. The Zn–Al based photocatalysts were stable and after three cycles provided an almost constant percentage of photodegradation [36].
The presence of compounds acting as scavengers, i.e., benzoquinone, triethanolamine, isopropanol and silver nitrate(V), made it possible to determine which scavengers disturb the equilibrium of photocatalytic reactions and which radicals take part in the photocatalysis reaction, making it possible to predict the mechanism of this process. Different scavengers were used individually in the photocatalytic reaction to quench a specific reactive species. It was observed that the presence of TEA resulted in a reduction in photodegradation to the highest extent, as well as an inhibition of \( \cdot \)O\(^2\)\(^-\) radicals causing a decrease in the activity of the materials. This indicates that these radicals are involved in the photodegradation mechanism. The lack of a significant decrease in the removal efficiency of dye is associated with a significant proportion of sorption (Fig. 9).

The results indicate that the \( \cdot \)O\(^2\)\(^-\) radical and the presence of h\(^+\) holes increase the photocatalytic activity and both the \( \cdot \)O\(^2\)\(^-\) radical and the h\(^+\) holes are involved in the photodegradation mechanism of QY. In the study, it was confirmed that the Ni content increases the activity of the materials and...
the presence of Ni\textsuperscript{2+} ions effectively enhance the activity of the materials. It is suggested that nickel acts as a dopant to the LDH framework, which can capture photogenerated electrons and suppress their recombination, increasing the lifetime of the photocatalyst. However, nickel at higher concentrations does not act on the trapping sites but acts on the electron–hole recombination centres, hence the highest activity was obtained for materials with 0.5 mol Ni/mol Zn addition.

Ni\textsubscript{Zn}Al LDH + hv \rightarrow Ni\textsubscript{Zn}AlLDH (e\textsuperscript{−} + h\textsuperscript{+})

Fig. 7 Photodegradation efficiency of quinoline yellow (QY): without presence of photocatalyst, in presence of Zn–Al LDH and Ni0.5–Zn–Al LDH nanoparticles in different source of light: incandescent light with a Kelvin colour temperature of 2700 K, halogen light with a Kelvin colour temperature of 4000 K, white light with a Kelvin colour temperature of 6500 K and UV light with a Kelvin colour temperature of more than 12000 K (time = 60 min, m = 50 mg, V\textsubscript{dye} = 200 cm\textsuperscript{3}, C\textsubscript{0,dye}=100 mg/dm\textsuperscript{3})

Fig. 8 Photodegradation efficiency of quinoline yellow (QY) in series of cycles of photocatalysts under UV light: a Zn–Al LDH, b Ni0.5–Zn–Al LDH (time = 60 min, m = 50 mg, V\textsubscript{dye} = 200 cm\textsuperscript{3}, C\textsubscript{0,dye}=100 mg/dm\textsuperscript{3})

When Ni0.5–LDH is exposed to UV light, e\textsuperscript{−}-h\textsuperscript{+} pairs are generated. The photogenerated holes move to the catalyst surface and react with water and OH\textsuperscript{−} ions to give \textbullet OH radicals. Concurrently, to a greater extent, electrons can react with oxygen adsorbed on the catalyst surface to form the superoxide \textbullet O\textsubscript{2}\textsuperscript{−}. The \textbullet O\textsubscript{2}\textsuperscript{−} radicals are highly reactive forms that, when acting on QY, cause its gradual degradation to simple molecules [37, 38]. On the other hand, photogenerated electrons reduce Ni\textsuperscript{3+} present on the catalyst surface (electron trap), promoting charge separation and producing h\textsuperscript{+} accumulation. To recover the oxidized form of Ni\textsuperscript{3+}, the captured e\textsuperscript{−} are transferred towards H\textsuperscript{+} adsorbed on the surface and lead to the formation of H\textsubscript{2}. Qi et al. analysed the effect of nickel addition in LDH structure, and suggested that photogenerated electrons are gradually reducing Ni\textsuperscript{3+} to Ni\textsuperscript{2+}, promoting charge separation and producing accumulation of h\textsuperscript{+}, which can move towards OH\textsuperscript{−} adsorbed and produce \textbullet OH [39]. Sun et al. proposed a comparable mechanism for a material based on double layered hydroxides consisting of zinc, nickel, and cobalt deposited on NiMoO\textsubscript{4} nanoparticles. The O\textsubscript{2} and H\textsubscript{2}O adsorbed on the surface of the nanoparticles, reacting with electron–hole pairs, are transformed into \textbullet O\textsubscript{2}\textsuperscript{−} superoxide radicals and hydroxyl radicals,
which directly react with organic dyes [40]. The proposed mechanism involving the reaction sequence is illustrated in Scheme 1.

4 Conclusion

This paper presents processes for the preparation of LDH nanoparticles modified with Fe, Ni, Cu and Co hydroxides using batch precipitation processes. The materials after modification with Ni(OH)₂ exhibited high photocatalytic activity and high sorption capacity towards quinoline yellow. QY photocatalysis studies allowed the determination of QY removal efficiency over 99%. Cyclic analysis of the materials revealed a decrease in the sorption contribution to QY removal processes, increasing the photocatalytic activity. This demonstrates the applicability of Ni₀.₅–Zn–Al LDHs as photocatalysts in organic compound removal processes.

Funding This research did not receive any specific Grant from funding agencies in the public, commercial, or not-for-profit sector.

Declarations

Conflict of interest The authors report no declarations of interest.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

References

1. X. Feng, Z. Yu, R. Long, X. Li, L. Shao, H. Zeng, G. Zeng, Y. Zuo, Sep Purif Technol 253, 117525 (2020)
2. A.L. Nuzhdin, M.V. Bukhtiyarova, G.A. Bukhtiyarova, J. Chem. Technol. Biotechnol. 95, 3292 (2020)
3. I. Clark, R.L. Gomes, C. Crawshaw, L. Neve, R. Lodge, M. Fay, C. Winkler, M. Hull, E. Lester, React. Chem. Eng. 4, 663 (2019)
4. Z. Cao, B. Li, L. Sun, L. Li, Z.P. Xu, Z. Gu, Small Methods 4, 1900343 (2020)
5. R. Soltani, R. Pelalak, M. Pishnamazi, A. Marjani, A.B. Albadarin, S.M. Sarkar, S. Shirazian, Sci. Rep. 2021 (11), 1 (2021)
6. R. Rojas, G. Mosconi, J.P. Zanin, G.A. Gil, Appl Clay Sci 224, 106514 (2022)
7. T. Hu, Z. Gu, G.R. Williams, M. Strimaite, J. Zha, Z. Zhou, X. Zhang, C. Tan, R. Liang, Chem Soc Rev 51, 6126 (2016)
8. E. Abdollahi, A. Heidari, T. Mohammad, A.A. Asadi, M. Ahmadzadeh Tofighy, Sep Purif Technol 257, 117931 (2021)
9. Z. Yang, F. Wang, C. Zhang, G. Zeng, X. Tan, Z. Yu, Y. Zhong, H. Wang, F. Cui, RSC Adv. 6, 79415 (2016)
10. Q. Fang, S. Ye, H. Yang, K. Yang, J. Zhou, Y. Gao, Q. Lin, X. Tan, Z. Yang, J. Hazard Mater 420, 126569 (2021)
11. G. George, M.P. Saravanakumar, Environ. Sci. Pollut. Res. 2018 (25), 30236 (2018)
12. B. Yuan, C. Zhang, Y. Liang, L. Yang, H. Yang, L. Bai, D. Wei, W. Wang, Q. Wang, H. Chen, Adv. Sustain. Syst. 5, 2000245 (2021)
13. Y. Zhang, J. Qin, X. Wang, Z. Chen, X. Zheng, Y. Chen, J. Environ. Manage 296, 113203 (2021)
14. A. A. Wani, A. M. Khan, Y. K. Manea, M. A. S. Salem, J. Rare Earths (2021).
15. T. Sadeghi Rad, A. Khataee, S. Sadeghi Rad, S. Arefi-Oskou, E. Gengec, M. Kobya, Y. Yoon, Ultrason Sonochim 82, 105875 (2022).
16. A. F. da Silva, J. L. da S. Duarte, L. Meili, Sep Purif Technol 264, 118353 (2021).
17. A.F. Morais, I.G.N. Silva, B.C. Lima, F.A. Garcia, D. Mustafa, ACS Omega 5, 23778 (2020)
18. M. Serdechnova, A.N. Salak, F.S. Barbosa, D.E.L. Vieira, J. Tedim, M.L. Zheludkevich, M.G.S. Ferreira, J. Solid State Chem. 233, 158 (2016)
19. S. Chakraborty, I. Sarkar, A. Ashok, I. Sengupta, S.K. Pal, S. Chakraborty, Appl. Therm. Eng. 141, 339 (2018)
20. Y. Wang, S. Guo, X. Xin, Y. Zhang, B. Wang, S. Tang, X. Li, Appl. Surf. Sci. 549, 149108 (2021)
21. S.A. Kulkarni, S.-S. Feng, Pharm. Res. 2013 (30), 2512 (2013)
22. S. Paikaray, M. A. Gomez, M. Jim Hendry, J. Essilfie-Dughan, Appl. Clay Sci. 101, 579 (2014).
23. C. Tessier, L. Guerlou-Demourgues, C. Faure, A. Demourgues, C. Delmas, J. Mater. Chem. 10, 1185 (2000)
24. R. Qin, Y. Pan, Z. Duan, H. Su, K. Ren, W. Wang, Y. Li, N. Xi, Y. Wang, L. Zhang, S. Han, J. Electrochem. Soc. 168, 070539 (2021)
25. X.-R. Ma, X.-Y. Wei, R. Dang, W. Guo, Y.-H. Kang, X. Li, Y. Gao, J.-J. Bai, Y. Zhang, Z.-F. Zhang, Y.-J. Ma, Z.-M. Zong, Appl. Clay Sci. 211, 106191 (2021)
26. M.M. Khan, N.H. Saadah, M.E. Khan, M.H. Harunsani, A.L. Tan, M.H. Cho, BioNanoScience 2019(9), 334 (2019)
27. V. Dubovoy, R. Subramanyam, M. Stranick, L. Du-Thumm, L. Pan, JoVE (J. Vis. Experim.) 2017, e55423 (2017)
28. L. Meili, P.V. Lins, C.L.P.S. Zanta, J.I. Soletti, L.M.O. Ribeiro, C.B. Dornelas, T.L. Silva, M.G.A. Vieira, Appl Clay Sci 168, 11 (2019)
29. R. Dang, X. Ma, J. Liu, L. Yan, W. Gao, J. Li, B. Chen, 24, 1 (2016). https://doi.org/10.1080/09276440.2016.1180733
30. A. Nait-Merzoug, O. Guellati, S. Djaber, N. Habib, A. Harat, J. El-Haskouri, D. Begin, M. Guerioune, Appl. Sci. 2021(11), 8899 (2021)
31. F. Zhang, L. Guo, S. Xu, R. Zhang, Langmuir 31, 6704 (2015)
32. X. Li, M. Fortunato, A.M. Cardinale, A. Sarapułova, C. Njel, S. Dsoke, J. Solid State Electrochem. 2021(1), 1 (2021)
33. M. Richetta, L. Digiamberardino, A. Matteocci, P.G. Medaglia, R. Montanari, R. Pizzoferrato, D. Scarpellini, A. Varone, S. Kaciulis, A. Mezzi, P. Soltani, A. Orsini, Surf. Interface Anal. 48, 514 (2016)
34. A. Razzaq, S. Ali, M. Asif, S.-I. In, Catalysts 2020(10), 1185 (2020)
35. L.S. Li, R. Mehedi, M. Malmivirta, P. Paturi, M. Lastusaari, M.M. Dîrîtu, Y. Garcia, P. Fardim, Appl. Clay. Sci. 132–133, 641 (2016)
36. K. Abderrazek, F.S. Najoua, E. Srasra, Appl. Clay Sci. 119, 229 (2016)
37. L. Zhang, C. Hua Dai, X. Xiu Zhang, Y. Nian Liu, J. Hui Yan, Trans. Nonferrous Metals Soc. China (Engl Ed) 26, 2380 (2016).
38. X. Wang, F. Wu, Y. Lu, Z. Huang, N. Zhu, C. Lin, Z. Dang, Sep. Purif. Technol. 132, 195 (2014)
39. M. Qi, L. Fan, Y. Shen, H. Zou, X. Tian, D. Liu, S. Li, J. Nanosci. Nanotechnol. 18, 753 (2018)
40. Y. Sun, J. Li, L. Zhang, B. Jiang, X. Yang, N. Yang, F. Peng, M. Xu, X. Xiao, Sep. Purif. Technol. 259, 118116 (2021)

**Publisher's Note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.