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**Photocatalytic removal of phenol and methylene-blue in aqueous media using TiO₂@LDH
clay nanocomposites**

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Abstract: Herein we report the formation of a series of nanocomposites composed of LDH structures and TiO₂ with anatase crystal phase. The structure of the LDH clay was modulated by the insertion of different di-, tri- or tetravalent cations, like Zn²⁺, Cu²⁺, Al³⁺, Fe³⁺ or Ti⁴⁺, within the brucite-like sheets. Afterwards, the anatase seeds were deposited onto the LDH clays, obtaining new nanocomposite systems with tailored photocatalytic activity. In this way the photoresponsive properties of the final nanocomposites were shifted from the UV to the visible range of the solar spectrum. The obtained nanocomposites were tested for the degradation of different organic pollutants, like phenol and methylene blue, under UV and visible light in aqueous media with different pH. The kinetic study showed that the TiO₂@LDH nanocomposites are efficient for the phenol (and its intermediary species Catechol and Hydroquinone) and methylene blue photocatalytic degradation under both UV and Vis light illumination.

Keywords: TiO₂@Layered Double Hydroxides, Nanocomposites, Phenol, Methylene Blue, Photocatalysis

1. Introduction

Removal of pollutants from industrial process wastewaters has driven considerable research efforts as the amount and the quality of freshwater available in the world continues to decrease. Chemical industry generate a wide variety of highly toxic organic wastes [1, 2]. Physical and chemical properties of wastewater vary depending on the location of the field, the rock types with which it is in contact, and the type of produced hydrocarbons. The most significant pollutants of the produced water are oil and grease, salts that have been dissolved and poly-aromatic hydrocarbons (e. g. phenol and its derivatives). Phenol and phenolic compounds are known as human carcinogenic and are of considerable health concern, even at low concentrations [3, 4].

Cationic dyes, such as methylene blue, are widely used in the textile industry or as antimicrobial agents, but when present in the aqueous ecosystems they are highly toxic, persistent, carcinogenic and mutagenic [5, 6].

The treatment of industrial wastewaters for removal of the organic compounds is nowadays an important aspect of environmental technology. Semiconductor photocatalysis may be considered as one of the most promising technologies because it represents an easy way to utilize the energy of either natural sunlight or artificial indoor illumination, and thus abundantly available everywhere in the world [7].

Photocatalysis takes advantage of the high reactivity of the HO[•] radicals in driving oxidation processes which are suitable for achieving complete mineralization of even most persistent

and less reactive pollutants. It also requires the use of nanocrystalline semiconductors as photocatalysts, which initiate interfacial redox reactions [8].

TiO₂ nanoparticles have been widely used for the photocatalytic degradation of organic molecules and nowadays it received the greatest attention due to its strong oxidation power, high stability and low cost production [9].

This semiconductor photocatalyst generates electrons and hole pairs (e^-/h^+) upon irradiation with light. Nevertheless, the recombination of holes and electrons or agglomeration of the fine nanoparticles which may lead to a decreased photocatalytic activity are, among others, current issues to be improved for practical applications. Therefore, it is especially interesting to support TiO₂ nanoparticles on suitable substrates which may offer the opportunity not only to improve its performance but also to form new stable compounds which lead to totally different physical and chemical properties from the individual components [10].

The layered double hydroxides (LDHs) have received much attention in the last decades due to their multifunctional properties. LDHs are host-guest materials consisting of positively charged metal hydroxide sheets with intercalated anions and water molecules. The structure of these materials is derived from the brucite structure in which the divalent cations are isomorphically substituted by the trivalent cations. They are represented by the general formula $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+} A^{n-}_{x/n} \cdot mH_2O$, where the divalent M^{II} and trivalent M^{III} cations may be Mg^{2+} , Zn^{2+} , Ni^{2+} , Cu^{2+} , Al^{3+} , Fe^{3+} , Ti^{4+} , and the A^{n-} can be almost any organic or inorganic anion [11, 12].

In particular, the LDH-type structures can be easily prepared with large flexibility for metal cations as well for the intercalated anions, thus a large variety of photocatalytic systems can be obtained deposition in order to overcome many of the drawbacks encountered when

using pure TiO_2 powders and achieve high photocatalytic efficiencies [4]. The layered structure may improve efficiency by inducing electron transfer, preventing recombination of $e^- - h^+$ pairs and avoiding the agglomeration of the nanoparticles. From the point of view of economic feasibility, the LDH-type materials represent a very appealing alternative of use as support materials for the TiO_2 deposition. These materials are obtained by a very easy co-precipitation method, which involve the use of only inorganic precursors without the need of post-synthetic treatments, e.g. calcination. At present, these materials are used as plastic additives and halogen scavengers at industrial scale, therefore it can be considered that they are economically feasible to be prepared. Several works are devoted to the use of LDHs, mainly containing MgAl- [13, 14] or ZnAl- [15] cation pairs in the brucitic layers, as support materials for TiO_2 nanoparticles. However, up to our knowledge, there is no report on the formation of such nanocomposites in which the cationic composition is altered within the LDH sheets to create heterojunction photocatalysts with enhanced properties.

The aim of this work is to design heterojunction nanocomposites by the deposition of TiO_2 nanoparticles on modified LDHs and to investigate if the cations within the LDH matrices can play a role in the degradation process. In this regard, the structure of the LDH clay is modulated by the insertion of different di-, tri- or tetravalent cations, like Zn^{2+} , Cu^{2+} , Al^{3+} , Fe^{3+} or Ti^{4+} , within the brucite-like sheets. The study will focus on the structural characterization as well as and the catalytic performances for the phenol photodegradation of the obtained TiO_2 @LDH clay nanocomposites.

2. Experimental procedures

The synthesis strategy of the TiO₂@LDH clay nanocomposites is realized in three steps: the LDH clay synthesis, the hydrothermal synthesis of the TiO₂ anatase seeds and finally the TiO₂ seeds deposition onto the layered clays.

2. 1. LDH matrices synthesis

Several LDHs matrices having different cation compositions in the brucite-like sheets, e. g. Zn²⁺, Cu²⁺, Al³⁺, Fe³⁺ or Ti⁴⁺, were synthesized by the widely used co-precipitation route at constant pH. The synthesis involved the slow mixing of the precursor salt solutions (1M in total) with the basic mixture of NaOH/Na₂CO₃ (1M in total) while maintaining constant pH values depending on the cationic species. The resultant precipitates were aged at 80°C under magnetic stirring for 18h, separated by centrifugation, washed thoroughly with distilled water and dried at 80°C overnight. In this way, four LDH matrices were prepared and denoted ZnAl-LDH (synthesis pH = 7.5, Zn/Al = 3/1), CuZnAl-LDH (synthesis pH = 7.5, Cu/Zn/Al = 0.2/2.8/1), ZnFe-LDH (synthesis pH = 10, Zn/Fe = 3/1) and CuZnFeTi-LDH (synthesis pH = 9, Cu/Zn/Fe/Ti = 0.2/2.8/0.8/0.2).

2. 2. TiO₂ seeds synthesis

TiO₂ anatase seeds were synthesized by the controlled hydrolysis of titanium (IV) tetra-isopropoxide ethanol solution followed by the hydrothermal treatment at 80°C for 4h in a Teflon-lined autoclave. The resultant anatase seeds were recuperated by centrifugation, washed several times with distilled water, air-dried at room temperature and calcined at 400°C (1°/min, 4h).

2. 3. TiO₂@LDH nanocomposite synthesis

The corresponding $\text{TiO}_2\text{@LDH}$ nanocomposites were obtained by suspending appropriate amounts of anatase seeds and in 1g of fresh LDH support. After 48h of vigorous magnetic stirring at room temperature, the obtained suspensions were centrifuged and the separated nanocomposite materials were washed and dried in ambient conditions. In this way, four nanocomposites were prepared and denoted $\text{TiO}_2\text{@ZnAl-LDH}$, $\text{TiO}_2\text{@CuZnAl-LDH}$, $\text{TiO}_2\text{@ZnFe-LDH}$ and $\text{TiO}_2\text{@CuZnFeTi-LDH}$, with an intended TiO_2 loading degree of $\sim 25\text{wt}\%$.

Based on the XRD observations which will be discussed in the later section, an additional nanocomposite sample was prepared based on the ZnFe-LDH matrix and denoted $^{1/2}\text{TiO}_2\text{@ZnFe-LDH}$. For this material, an initial $\sim 12.5\text{wt}\%$ TiO_2 loading degree was used.

2. 4. Photocatalytic testing

The photocatalytic response of the as-prepared nanocomposites was evaluated for the degradation of phenol and methylene blue (MB) in aqueous solutions under both UV and Vis light irradiation and at different pH values. The pH of the reaction mixtures was adjusted using a 0.1M NaOH solution. In a typical experiment, appropriate amounts of catalysts were suspended into phenol or MB solutions (solid/liquid ratio of 1g/L), respectively, and stirred in dark for 30 to 60 min., depending on each adsorption capacities, in order to establish the adsorption/desorption equilibrium between the pollutant molecules and the catalyst surface. Afterwards, the suspensions were stirred under UV or Vis light irradiation, respectively. The photocatalytic batch set-up for both UV and Vis light irradiations are included in Figure S1 (*Supplementary File*). The UV-light source was a 100 W Hg lamp (Sylvania Par 38, 365 nm) and the Vis-light source was a Halogen lamp of max. 150 W (CIXI ZHONGFA LAMPS CO., LTD). As the maximum of absorbance is shifted as a function of pH, especially in the case of phenol, full scale absorbance spectra of the irradiated solutions

were measured. It is also important to mention that the absorbance at two different wavelengths was investigated, e.g. 270 nm for pH 6 and 290 nm for pH 9. The evolution of the photocatalytic degradation in terms of absorbance and not further transformed in concentration using the Lambert Beer's Law is presented. Accordingly, the degradation of the organic pollutants in the aqueous solution was followed by measuring the absorption profiles in the range of 190 – 500 nm for the phenol removal tests, and in the range of 450 – 750 nm for the MB removal tests, respectively, using a Thermo-electron Evolution 500 UV-Vis Spectrometer against water as reference.

2. 5. Characterization techniques

The chemical compositions of the obtained materials as well as the TiO₂ loading degrees were determined by electron probe microanalysis measurements (EPMA) using a JEOLJXA-733 apparatus.

Structural characterization was obtained by X-ray Diffraction (XRD), Raman and UV-vis DR Spectroscopy techniques, while the porous characteristics were investigated by N₂ sorption measurements.

X-ray diffraction patterns were recorded on a PANalytical X'Pert PRO MPD diffractometer with filtered CuK α radiation; measurements were done in the 2 θ mode using a bracket sample holder with a scanning speed of 0.04°/4 s in continuous mode.

Raman spectra were measured on a Nicolet Nexus 670 bench equipped with a Ge detector in a 180° reflective sampling configuration using a 1064 nm Nd:YAG laser.

UV-vis-DR spectra were obtained at room temperature on a NICOLET EVOLUTION 500 UV-VIS Spectrometer, with a diffuse reflectance accessory using KBr standard white as reflectance.

Porosity and surface area studies were performed on a Quantachrome Quadrasorb-SI automated gas adsorption system using nitrogen as the adsorbate at liquid nitrogen temperature (-196°C). All the samples were outgassed under vacuum for 16 h at room temperature before the adsorption measurements. The surface area was calculated using the BET method in the range of relative pressure 0.05–0.35. The pore size distributions were deduced from the adsorption branches of the isotherms using the Barrett–Joyner–Halenda (BJH) method. The total pore volumes were calculated from the amount of N₂ vapor adsorbed at a relative pressure of 0.95.

3. Results and Discussions

3. 1. Structural characterization

The XRD patterns of the as-synthesized LDH matrices as well as after the TiO₂ seeds deposition towards the formation of the TiO₂@LDH heterojunction nanocomposites are presented in Figure 1. The XRD patterns recorded for the pure LDH matrices reveal the formation of typical layered structure of which crystallization degree is related directly with the type of cations inserted within the brucite-like network. The peaks assigned for the (003) plane in all XRD patterns indicate the 3R layer stacking order similar to that of CO₃⁻ containing LDHs [5]. Only in the case of the Fe-containing samples (Figure 1C and D) this peak is shifted to lower 2θ values indicating the formation of NO₃⁻-containing LDH material [16], although we do not exclude the carbonate presence in these materials as a small fraction of interlayer species. This preference for nitrate anions of the iron containing LDH

materials was previously reported by Mantilla et al. where mainly nitrate interlayer species were found for materials with the highest iron content into a ZnAl lattice [17].

Figure 1.

The reflections of the (003) and (110) planes were used to further calculate the unit cell parameters of the layered structure (see Table 1) using the equations $c = 3d_{003}$ and $a = 2d_{110}$, where c corresponds to three times the interlayer distance and a is the average metal-metal distance in the brucite-like sheets network [11].

Table 1

It is also important to mention that the insertion of the Cu^{2+} cations within the layered network leads to distortion of the octahedral units around the Cu sites due to the presence of the Jahn-Teller effect with a concomitant decrease in the intensity of the main XRD reflections [18-20]. This effect is observed in the CuZnAl-materials (Figure 1B) and becomes more evident in the CuZnFeTi-materials (Figure 1D) for which a lowered intensity of the (003) plane may be observed and can be correlated with the presence of the Cu^{2+} cations and consequently, distortions of the octahedral units. Other difference of the c unit cell parameters may be assigned to different electrostatic interactions of the positive brucite-like layers having different compositions and interlayer anionic species.

At the same time, the variation of the a unit cell parameter demonstrates the successful insertion of the foreign cations within the layered network. This observation may be correlated with the different ionic radii, different M-O bond length respectively, in the octahedral units. Consequently, this value varies slightly from the ZnAl-system towards the CuZnAl- and ZnFe-systems ($r_{\text{Zn}^{2+}} = 0.074 \text{ nm} \sim r_{\text{Cu}^{2+}} = 0.073 \text{ nm}$, $r_{\text{Al}^{3+}} = 0.054 \text{ nm} \sim r_{\text{Fe}^{3+}} = 0.055$

nm) and increases towards the formation of the CuZnFeTi-multicomponent system ($r_{\text{Ti4+}} = 0.061 \text{ nm}$).

The TiO_2 anatase seeds are deposited onto the highly hydroxylated brucite-like sheets via interface affinity between the two phases. The crystallite size of the TiO_2 seeds is 6.8 nm as calculated with Scherrer equation [21]. The XRD patterns recorded for the $\text{TiO}_2@\text{LDH}$ nanocomposite materials show characteristic reflections for both LDH and TiO_2 with anatase crystal phase. It is important to note that the a unit cell parameter maintain the same values as before the anatase seeds deposition suggesting the preservation of the LDH structure during the nanocomposites formation. For the $\text{TiO}_2@\text{ZnFe-LDH}$ nanocomposite, the XRD pattern does not show the characteristic reflections for the LDH phase indicating the suppression of the layered structure. In this case, an additional nanocomposite was prepared by the deposition of half on TiO_2 seeds, sample denoted as $^{1/2}\text{TiO}_2@\text{ZnFe-LDH}$, where characteristic reflections starts to appear also for the LDH phase.

The N_2 sorption measurements revealed all the obtained materials are endorsed with mesoporous characteristics. After the anatase seeds deposition, the specific surface area values decrease indicating the immobilization of the anatase seeds onto the mesoporous structure of the LDH matrices (Table 1). The N_2 sorption isotherms and representative SEM images are included in Figure 2. The effective loading of the TiO_2 seeds was evaluated using the EPMA measurements and the results are given in Table 1.

Figure 2.

In general, the LDH-type materials are characterized by external surface mesoporosity since the N_2 molecular diameter is larger than the interlamellar space of carbonate-containing solids, therefore the measured pore volume corresponds to interparticle pores [22]. All the

N₂ sorption isotherms are typical Type II, where the adsorption does not reach a plateau at high relative pressures. Their full adsorption/desorption profile give rise to a H₄ hysteresis loop with a delayed desorption up to low relative pressures. This is an indication of formation of very small slit-shaped pores. Microporous characteristics are also observed for the iron containing nanocomposites (Figure 2c and d) as indicated by the increase of the volume adsorbed at low relative pressure. The shape of these isotherms is characteristic for porous adsorbents which contain pores with a wide range of sizes which cross the micropore-mesopore boundary. This might be due to the presence of Fe³⁺ cations which are the only the charge generating cations leading to very small interconnected agglomerate particles, which exhibit significant external area (Table 1) [23]. The insertion of tetravalent Ti⁴⁺ cations also in the LDH network, e. g. sample TiO₂@CuZnFeTi-LDH, leads to the changes of the shape of the hysteresis loop into H₃ which may indicate the formation of aggregated particles containing slit-shape pores [23]. The calculated pore diameters are in the range of 4.8 - 12 nm.

Low frequency Raman measurements were realized to obtain additional evidence on the presence of the two phases in the nanocomposites as well as the TiO₂ crystallization form. Due to high fluorescence and heating effect of the colored samples, only the Raman spectra of the ZnAl-systems in comparison with the pure as-prepared TiO₂ seeds are given (Figure 3 A).

Figure 3.

The well resolved Raman bands at 148 cm⁻¹, 399 cm⁻¹, 519 cm⁻¹ and 630 cm⁻¹ are generally assigned to the anatase crystallization form of TiO₂ [24, 25], while the Raman active carbonate vibration at 1050 cm⁻¹ may be correlated with the LDH-type material [10, 26]. The

Raman observations are in agreement with the XRD data showing that the as-prepared nanocomposites consist of well crystallized anatase nanoparticles accommodated within LDH-type matrices.

The evaluation of the band gap energy for the TiO_2 @LDH nanocomposites was realized by measuring the UV-vis DR spectra, extrapolating the sharply rising and horizontal portions and defining the edges as the wavelengths of the intersection [27]. The calculated band gap energies are also given in Table 1. The UV-vis DR spectra indicate that the insertion of Cu^{2+} , Fe^{3+} and Ti^{4+} cations within the LDH matrices induce the shift of the photoresponsive properties from the UV to the visible range of the solar spectrum. This may represent an additional advantage in using the LDH-type materials as support for the immobilization of the TiO_2 nanoparticles and formation of such nanocomposite materials with mesoporous features. In such nanoarchitectures the TiO_2 seeds are well-dispersed on the LDH support without aggregation leading to an increased surface of anatase, which are the active sites for photocatalytic reactions and therefore, adequately exposed to the target organic molecules to be degraded. Another important aspect is that the band gap energy is decreased in comparison with the pure TiO_2 anatase seeds enabling the photocatalytic response in the visible region of the solar irradiation. On the other hand, such low band gap values would decrease also the charge separation lifetimes. In this case, the foreign cations which are well distributed within the brucite-like network are playing an important role. These key cations can act as centers for charge separation and thus enhancing the catalytic efficiencies by enabling the heterojunctions between the TiO_2 active sites and the LDH sheets and therefore suppressing the recombination. The formation of such unique heterojunction nanocomposites may represent an alternative of the TiO_2 supported for example on siliceous mesoporous materials which are further doped with transition metals for visible light

photocatalysis. These nanocomposite systems are easily designed by the simple deposition of TiO_2 seeds on one support which combines the porous features as well as UV and/or Visible photoresponsive properties offered by the highly distributed key cations within the LDH configuration. Consequently, high photocatalytic activities are expected for the TiO_2 @LDH heterojunction nanocomposites.

3. 2. Photocatalytic study

The photocatalytic activity of the obtained TiO_2 @LDH nanocomposites was studied for the degradation in UV and Vis light irradiation of two types of organic pollutants, e. g. phenol as a representative for its class of aromatic hydrocarbons, and methylene blue as a representative molecule for its class of dyes, respectively.

Physical and chemical properties of the wastewaters are varying significantly depending on the location of the field, the rock types with which it is in contact and the type of pollutants. For example, methylene-blue (MB) is a cationic dye and accordingly, at high pH values its adsorption and degradation may be favored by negatively charged catalytic surfaces.

On the other hand, in different pH media the catalysts surfaces are also modified from the point of view of the external electric layer. The present catalytic active sites are the seeds of TiO_2 with anatase crystal structure which manifest the zero point charge (pzc) at pH 6.8 [28, 29]. This means that when placed in high pH media, its surface becomes negatively charged which may favor the adsorption and consequently the decomposition of the phenol or methylene blue molecules.

Before photocatalytic tests, adsorption studies were performed at different pH values for both types of test molecules in order to verify the adsorption capacities of the

nanocomposites as well to demonstrate that the pollutants removal is realized by a photocatalytic mechanism. Moreover, in order to improve the efficiencies towards total removal of phenol and MB the photocatalytic reactions were conducted in different pH values, e. g. neutral and basic media.

3. 2. 1. Adsorption and photocatalytic degradation of phenol

Adsorption and photocatalytic experiments were carried out using all the $\text{TiO}_2\text{@LDH}$ nanocomposites using the same phenol concentration (10mg/L) and catalyst dose (1g/L) but at different pH values. The photodegradation of phenol does not occur in one step, but several intermediary aromatic and aliphatic molecules are produced before complete degradation towards carbon dioxide and water. The degradation profile was followed at two different wavelengths since the UV-Vis absorption profile measured in the range of 200-400 nm indicated the bathochromic shift towards higher wavelength (e. g. 290 nm) when basic media was used (as shown in Figure 4, C and D).

The representative adsorption study and the total removal efficiency as a function of pH using UV and Vis light irradiation are shown in Figure 4. Adsorption studies were realized for all types of nanocomposites at different initial pH values of the phenolic aqueous solution and reveal that the catalysts adsorb preferentially the phenol molecules in basic media than at neutral pH (Figure 4A). The observed adsorption behavior may be correlated with the changes in the electrical double layer of the solid-liquid interface as we previously observed for this type of nanocomposites [10].

The total degradation efficiencies for the obtained $\text{TiO}_2\text{@LDH}$ nanocomposites are presented in Figure 4B. It can be observed that the initial pH value strongly influences the photocatalytic efficiency. At higher pH values than phenol pKa (9.89), the phenoxy radical is

formed which leads to the rapid formation of hydroquinone as a primary intermediary product. It was also reported that the generated phenoxy radical can polymerize via C-C or C-O coupling leading to dimeric products [30, 31]. In any case the generated $\text{HO}^\bullet$ radicals have an oxidizing power much higher than that of the produced intermediary species and leads to ~90% efficiency of phenol within around 5 h of UV and Vis light irradiation.

Figure 4.

The presence of Cu^{2+} and Fe^{3+} cations within the LDH network leads to a positive effect when the photocatalytic tests are realized under Vis light irradiation. This may be well correlated with the UV-vis DR observations which indicated the enabling of the photoresponsive properties towards visible range of the solar spectrum when these cations are present even in such low concentrations in the LDH matrix. For these nanocomposites, high removal efficiencies are obtained even at pH 6 under UV irradiation (up to 75% phenol removal for the $\text{TiO}_2@\text{ZnFe-LDH}$ sample). Furthermore, the Cu^{2+} and Fe^{3+} containing nanocomposites showed up to 90% efficiency for phenol removal under visible light irradiation (Figure 4B, b, c and d). It is also important to mention that the $\text{TiO}_2@\text{CuZnAl-LDH}$ nanocomposite shows higher removal efficiency when irradiated in Vis light conditions than the $\text{TiO}_2@\text{CuZnFeTi-LDH}$ sample. This may be correlated with the higher crystallinity of the $\text{TiO}_2@\text{CuZnAl-LDH}$ nanocomposite as observed in Figure 1B as well as higher intensity of the absorbance in the UV-vis DR spectra (Figure 3B).

3. 2. 2. Photocatalytic degradation of methylene blue

The best photocatalytic activity in both UV and visible light for phenol removal was obtained for the $\text{TiO}_2@\text{ZnFe-LDH}$ material. Therefore, this nanocomposite was further tested for the photodegradation of methylene blue (MB) dye and compared with its correspondent

TiO₂@ZnAl-LDH nanocomposite. The photocatalytic experiments were realized using the same methylene blue concentration (1×10^{-4} M) and catalyst dose (1g/L) but at different pH values. The adsorption kinetic profiles and the removal efficiency of the MB as a function of the initial pH using selected nanocomposites and UV or Vis light irradiation are illustrated in Figure 5. The adsorption studies show an increase of the MB adsorption onto the nanocomposite surfaces at higher pH medium (Figure 5A) and this behavior may be attributed to an increased electrostatic interaction of the cationic dye and the negatively charged TiO₂ nanoparticles in the nanocomposites. Consequently, the total removal efficiency is also increased at high pH values. The TiO₂ surface is negatively charged in basic media favoring MB adsorption and decomposition. The ^{1/2}TiO₂@ZnFe-LDH nanocomposite, which showed better structural characteristics was also tested for its photocatalytic properties. This nanocomposite is loaded with only half of the TiO₂ amount as compared with its homologue TiO₂@ZnFe-LDH material, but it manifests higher photocatalytic activity in terms of amount of photocatalytic active sites per mass of solid used in a reaction. When tested for its performances in visible light irradiation, around 55% removal efficiency was obtained at pH 10.

Figure 5.

Overall, these nanocomposites on which the TiO₂ with anatase crystal phase is supported on the LDH-type matrix possess high photocatalytic activity in both UV and visible light, and the removal efficiency can be easily manipulated by controlling the nature of the cations within the layered sheets. Another advantage of using such nanocomposites stands in the separation step at the end of the catalytic tests. It is well known that the use of commercially available TiO₂ photocatalysts, e. g. P25, leads to difficulties in the separation step at the end

of the catalytic process. These nanocomposites are based on layered clays and can be separated by natural sedimentation within minutes at the end of the process.

The performances of the obtained nanocomposites were benchmarked with TiO₂ P25 commercial photocatalyst for both types of pollutant molecules. It can be observed that the photocatalytic performances of TiO₂@LDH nanocomposites under UV irradiation are comparable with that of P25. An important aspect is that the TiO₂ P25 is characterized by a band gap energy of 3.2 eV which makes it active only under UV irradiation. The TiO₂@LDH nanocomposites in which the brucite-like sheets contain highly distributed Cu²⁺ or Fe³⁺ cations allow the possibility to promote the photodegradation of the organic pollutants under the natural sunlight irradiation as it can be observed from the results presented in Figures 4B and 5B. Therefore, it may be concluded that the LDH matrices play also the major role in the degradation process.

4. Conclusions

A series of TiO₂@LDH-type nanocomposites were prepared by a simple deposition procedure of anatase TiO₂ seeds on a layered support. Increased mesoporosity and spectral features were obtained by modulating the brucite-like sheets composition and insertion of Cu²⁺, Fe³⁺ or Ti⁴⁺ cations within the LDH network. The obtained nanocomposites show high photocatalytic activity, comparable with TiO₂-P25, in both UV and visible light in basic environment due to the negatively charged TiO₂ surface sites which has a positive effect on the adsorption of the phenol and MB dye molecules.

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Table caption

Table 1. Structural and porosity characteristics of the LDH, TiO_2 and $\text{TiO}_2@\text{LDH}$ materials.

Table 1.

Sample	a, nm	c, nm	S_{BET} , m ² /g	TV_p , cm ³ /g	^a wt%TiO ₂	E _g , eV
ZnAl-LDH	0.307	2.33	25	0.145	-	-
TiO ₂ @ZnAl-LDH	0.307	2.39	21	0.054	27	3.16
CuZnAl-LDH	0.308	2.34	5	0.018	-	-
TiO ₂ @CuZnAl-LDH	0.308	2.65	36	0.087	23	2.9
ZnFe-LDH	0.307	2.06	230 ($\mu\text{S} = 187$)	0.190	-	-
TiO ₂ @ZnFe-LDH	-	-	199 ($\mu\text{S} = 65$)	0.180	26	1.85
^{1/2} TiO ₂ @ZnFe-LDH	0.307	2.06	202 ($\mu\text{S} = 139$)	0.180	11	1.88
CuZnFeTi-LDH	0.310	2.07	140	0.393	-	-
TiO ₂ @CuZnFeTi-LDH	0.310	2.08	133	0.340	24	2.13
TiO ₂	-	-	86	0.116	100	3.24

S_{BET} – specific surface area calculated using the BET method, TV_p – total pore volume measured at p/p_0 of 0.95, ^a Calculated based on the EPMA results, E_g – band gap energy.

Figure caption

Figure 1. The XRD patterns of the as-synthesized LDH matrices, TiO_2 @LDH nanocomposites compared with the pure TiO_2 seeds (@ - anatase crystal structure).

Figure 2. N_2 adsorption-desorption isotherms (left) and the corresponding SEM images (right) of (a, a') TiO_2 @ZnAl-LDH, (b) TiO_2 @CuZnAl-LDH, (c, c') TiO_2 @ZnFe-LDH, (d) $^{1/2}\text{TiO}_2$ @ZnFe-LDH and (e, e') TiO_2 @CuZnFeTi-LDH nanocomposites.

Figure 3. Raman (A) and UV-vis DR (B) spectra of the as-synthesized materials.

Figure 4. A: Adsorption study of phenol at different pH values on TiO_2 @ZnAl-LDH sample; B: photocatalytic efficiencies of (a) TiO_2 @ZnAl-LDH, (b) TiO_2 @CuZnAl-LDH, (c) TiO_2 @ZnFe-LDH, (d) TiO_2 @CuZnFeTi-LDH samples compared with (e) P25 for phenol at different pH and UV or Vis light irradiation (phenol concentration 10mg/L, catalyst dose 1g/L). UV-vis absorption profiles of the phenolic solution during the photodegradation process using TiO_2 @ZnFe-LDH nanocomposite at C: pH = 6/UV light and D: pH = 10/UV light irradiation.

Figure 5. A: Adsorption study of MB at different pH values on TiO_2 @ZnAl-LDH sample; B: photocatalytic efficiencies of (a) TiO_2 @ZnAl-LDH, (b) TiO_2 @ZnFe-LDH, (c) $^{1/2}\text{TiO}_2$ @ZnFe-LDH samples compared with (d) P25 for MB at different pH and UV or Vis light irradiation (MB concentration $1 \times 10^{-4}\text{M}$, catalyst dose 1g/L). UV-vis absorption and kinetic profiles of the MB solution during the photodegradation process using $^{1/2}\text{TiO}_2$ @ZnFe-LDH nanocomposite at C, C': pH = 6/UV light and D, D': pH = 10/UV light irradiation, respectively.

Figure

Figure 1.

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Figure 2.

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Figure 5.

Supplementary Interactive Plot Data (CSV)

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