Improvement of the optical and photocatalytic properties of ZnAl$_2$O$_4$: 1% La$^{3+}$, x% Pb$^{2+}$ nanoparticles synthesized by citrate sol-gel route

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Abstract

Samples of pure zinc aluminate (ZnAl$_2$O$_4$) and doped both with lead (Pb$^{2+}$) at different ratios (0, 0.5, 1, 1.5, 2 and 2.5% mol) and a constant amount of lanthanum (La: 1% mol), were prepared by the citrate sol-gel technique, and then annealed at 900°C for 2h. In order to study the structural, optical and thermal properties; different characterization methods were used, such as: powder X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDX), differential scanning calorimetry (DSC), TGA, Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy. The Analyzes by XRD revealed the presence of the cubic single phase ZnAl$_2$O$_4$ for all samples, with a crystallites size between 19 and 25 nm. These results were confirmed using FTIR, Raman spectroscopy and SEM. Also, photocatalytic study for different samples of ZnAl$_2$O$_4$ shows that they can be used like as photocatalyst and good adsorbents for degradation of Hexamethyl crystallized violet dye in aqueous solution.

Keywords: word; ZnAl$_2$O$_4$, nanoparticles, Sol-gel, doping, photocatalytic.

1. Introduction

Spinel ZnAl$_2$O$_4$, has a high thermal and chemical stability, a high mechanical strength and a low surface acidity [1, 2], its wide band gap energy (E$_g$~3.8 eV) [1, 3-7], its particle size, and large surface area, make it a material of choice for a variety of applications, such as heterogeneous catalysis and adsorption of molecules [8]. Also, zinc aluminate has been recently considered as a functional material in host luminescent applications [9]. Moreover, ZnAl$_2$O$_4$ has been widely employed as a good host phosphor material as a result of uniform particle and narrow size distribution [10]. For effective doping, rare earths or lanthanides are widely used as activators in luminescent materials due to high emission properties [4-7, 11-12]

On the other hand, adsorption is a technique that consists of fixing the pollutants on the surface of an adsorbent without altering the pollutant. It is very widely used as a refining treatment. Photocatalyst is also aims to eliminate organic micro pollution, but unlike adsorption, its ultimate goal is to degrade or even mineralize organic pollutants. In recent years, zinc aluminate has been largely used as a photocatalyst for degradation of organic pollutants in water such as dyes. In our work also tested it as an adsorbent to remove the HCV dye. The crystal violet dye was considered as a low biodegradable and
very persistent organic pollutant. Its presence in aquatic environments can be detrimental to animal and plant species as well as to the various microorganisms living in these waters. The absorption of the HCVs is maximal at the wavelength 590 nm. Therefore, in order to assess the effectiveness of the synthesized ZnAl$_2$O$_4$ powder and even what field it can be used in; the water treatment area was tested as a photocatalysts to purify the water from organic pollutants [9].

It is known that, zinc aluminate has the normal spinel structure and the chemical formula of AB$_2$O$_4$ in which Zn$^{2+}$ (A) ions occupy tetrahedral sites and Al$^{3+}$ (B) ions the octahedral sites. In general, A and B cations can reside on both T and M sites, thus giving rise to a variable disorder degree, which can be described using the inversion parameter $i$, defined as the fraction of the B cations at the T sites. The inversion parameter can therefore vary from 0, in the completely normal spinel $^T$A$^M$B$_2$O$_4$, to 1, in the completely inverse spinels $^1$B$^M$ (AB) O$_4$; while the value 2/3 is assuming for a completely random (i.e. disordered) cation distribution [17]. Many synthesis methods preparation of ZnAl$_2$O$_4$ have been reported, such as: hydrothermal [10, 18]; citrate [1, 19, 20], sol-gel [21-22], combustion [13, 23- 25], pyrolysis [14, 26], co-precipitation [15, 27- 29] and solvothermal [30-31]. While doping ZnAl$_2$O$_4$ was carried out with transition metals or rare earths depending on the intended application [6-7, 14, 32].

In this present study, we have used the citrate sol-gel method for preparing samples of pure ZnAl$_2$O$_4$ and dual doped by a constant concentration of La$^{3+}$ (1% mol) and x% mol Pb$^{2+}$ with different amounts of Lead (0, 0.5, 1, 1.5, 2, and 2.5% mol). The materials annealed at 900°C for 2h have been characterized for their structural and optical properties. In addition, we have prepared a sample ZnAl$_2$O$_4$ containing 50% by weight of ZnO in order to better characterize the effectiveness of the two purification methods, notably photocatalysis and adsorption.

2. Methods and Materials

2.1 Synthesis of ZnAl$_2$O$_4$

To prepare the ZnAl$_2$O$_4$ powder, 2.19 g of Zinc Acetate dihydrate (C$_4$H$_6$O$_4$Zn.2H$_2$O) was mixed with 20 ml of distillated water and stirred magnetically for 30 minutes. On the other hand, another solution contains 7.5 g of Aluminum nitrate nonahydrate (Al(NO$_3$)$_3$.9H$_2$O) and 20 ml of distillated water was prepared with the same preceding method. The two solutions were mixed well using the citric acid (C$_6$H$_8$O$_7$) as chelating
agent. Then the resulted mixture was dried on hot plate at 80°C during 90 minutes. The
doped ZnAl\(_2\)O\(_4\) solutions were prepared exactly like the pure one. A constant amount of
Lanthanum Acetate hydrate (La(CH\(_3\)CO\(_2\))\(_3\).H\(_2\)O) (1 % mol) was added in the first
solution of Zinc. On the other hand, different amount of Lead (II) Acetate trihydrate
(C\(_4\)H\(_6\)O\(_4\)Pb.3H\(_2\)O) was added to the second solution of Aluminum nitrate (0, 0.5, 1, 1.5,
2 and 2.5 % mol). After drying the mixture obtained, it is subjected to a heat treatment
at 900°C for 2h in an oven. Finally, we have seven samples called pure ZnAl\(_2\)O\(_4\), S0,
S1, S2, S3, S4 and S5 respectively.

### 2.2 Photocatalytic and adsorption

To test the reactivity of the two processes on the HCV molecules, a solution containing
HCV with concentrations equal to 5 mg/l and 0.1 g for each sample of ZnAl\(_2\)O\(_4\) powder
has prepared. The evolution of HCV was followed as a function of time of contact, by
the measurement of the absorption at 590 nm. In photocatalytic activity, a cylindrical
Pyrex photo reactor initiated by UV mercury lamp (350 W) placed in center of a closed
enclosure, the solution of HCV and the catalyst were stirred in the dark for 30 minutes
to establish the adsorption-desorption equilibrium. After each appropriate time interval,
5 ml aliquots was sampled and filtered using 0, 22 µm membranes filters (S-PAK), to
remove the solid phase thus allowing the analyze by spectrophotometer (SHIMADZU,
UV-1800).

### 2.3 Characterization

The obtained powder was characterized by X-ray diffraction using Cu\(_{Kα}\) radiation
Bruker (D8 Advance) X-ray diffractometer. The structural composition of powders was
studied using m-Raman spectrometer (Jobin-Yvon). Optical properties were analyzed
using UV–visible spectrophotometer (Shimadzu, UV-1800). The Morphological studies
of powders were carried out by Scanning Electron Microscopy (Philips XL30 S-FEG).
FT-IR analysis was carried away using KBr disc technique on a FT-IR spectrometer
Bruker IFS66v. EDX measurements have been performed with a Hitachi S-3000N
scanning electron microscope and the thermal analysis of dried gel was studied by STA
449 F3 Jupiter®.
3. Results and discussions

3.1. Powder X-ray diffraction

Figure 1.a shows the XRD diagrams of pure ZnAl$_2$O$_4$ and samples S0, S1, S2, S3, S4 and S5. All patterns show the characteristic diffraction peaks corresponding to (111), (220), (311), (400), (331), (422), (511), (440), (533), (642), (731) reflections of cubic ZnAl$_2$O$_4$ spinel structure (JCPDS No. 05-0669). These results show the existence of traces impurities such as ZnO on some samples. The degree of crystallinity is calculated from the XRD spectra of the samples:

\[
C (\%) = \frac{\text{Area of crystalline peaks}}{\text{Area of all peaks}} \times 100
\]

, and the results are presented in Table 1. The average size of the crystallites (D) was calculated from the five most intense X-ray diffraction peaks, using Scherrer’s formula (1), [7, 16-18].

\[
D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)
\]

Where \(\lambda\) is the wavelength of Cu-K\(\alpha\) (0.15406 nm), \(\beta\) is the full width at half maximum (FWHM) of the peak and \(\theta\) is the Bragg angle. We found average crystallites size between 19 and 25 nm for S2 and S5, respectively (Table 1). In addition, we noticed a slight shift of the peaks of the S0 sample towards the low angles compared to the pure sample of ZnAl$_2$O$_4$. This suggested that the increase in lattice parameter is most likely due to the presence of La$^{3+}$ in ZnAl$_2$O$_4$ system. Because, the ionic radius of La$^{3+}$ (1.04 Å) [27] is greater than those of the tetrahedral (Zn$^{2+}$ (0.60 Ǻ), Al$^{3+}$ (0.39 Ǻ)) and octahedral (Zn$^{2+}$ (0.74 Ǻ, Al$^{3+}$ (0.54 Ǻ)) sites of ZnAl$_2$O$_4$ system [19]. Similar results have been previous observed in the ZnAl$_2$O$_4$ doped by Lanthanides elements [11, 14, 18]. The most intense (220) and (311) diffraction peaks for all samples are illustrated in figure 1.b. We observe also that when Pb$^{2+}$ is added up to 1.5 % mol to the S0 sample, the shift of the most intense peaks is towards the large angles, then beyond this percentage of Pb$^{2+}$, the shift changes by meaning. Although the ionic radius of Pb$^{2+}$ (1.23 Å) [32] is greater than those of Zn$^{2+}$ and Al$^{3+}$, the Vegard's law is violated up to 1.5% mol. The lattice parameters (a) for all samples are presented in Table 1. The variation of the lattice parameter of the samples versus of the % Pb$^{2+}$ is represented by figure 1.c, and shows well the parabolic behavior relationship to Pb$^{2+}$mol %. This result
can be explained by the decrease in the electronic cloud of the outer layer of Pb$^{2+}$, due to its electronic interactions with a greater number of closer neighbors Zn$^{2+}$, which makes it smaller than the Zn$^{2+}$ ion. As the percentage of Pb$^{2+}$ is increased, the shrinkage must be smaller; therefore, the lattice parameter should be increase. We note a similar phenomenon was observed by S.V. Motlung and al. [33].

3.2 FTIR spectroscopy

The fig. 2 represents the IR spectra of the samples pure ZnAl$_2$O$_4$ and S0, S1, S2, S3, S4 and S5. We observe the same absorption bands in all spectra, such the broad band centered on 3400 cm$^{-1}$ and the band 1615 cm$^{-1}$. These are related to the OH stretching vibration and H$_2$O deformation vibration, respectively. Also, the presence of three absorption bands located at 643, (550-565) and 501 cm$^{-1}$ comes from the stretching and bending modes vibration of octahedral bonds (AlO$_6$) [34-36]. These bands are characteristic of the ZnAl$_2$O$_4$ spinel structure. The sharp absorption band at 2300 cm$^{-1}$ is due to the stretching vibration mode of CO$_2$. The adsorption of water and carbon dioxide from the atmosphere may be due to the very high specific surface area of these materials [37]. No other impurity phase is detected by FTIR spectra, and is in good agreement with the results obtained by XRD.

3.3 DSC and TGA

The behavior of the gel as a function of temperature was studied by continuous heating using simultaneously thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The thermal cycle applied under an atmosphere of neutral nitrogen consists of heating from ambient temperature to 1000 °C at a speed of 10 °C / min, followed by holding at this temperature for 10 minutes, and cooling to ambient temperature. The TGA and DSC pattern of pure ZnAl$_2$O$_4$ is record and depicted in fig.3. The TGA and DSC curves of all samples are almost similar. Thermo gravimetric analysis reveals that the thermal decomposition of precursors takes place in four stages (see fig.3.a): The first loss of mass (~14 %) is observed between room temperature and 210 °C. It probably corresponds to the dehydration of the gel (adsorbed water). A second mass loss (9 %), starts at 210 °C and ends at 310°C [38]. It can only be attributed to the decomposition of nitrates. The third stage reveals a significant loss of mass (~ 37 %) which is mainly due to the combustion of acetates and citric acid.
Finally, a weak mass loss (~ 8%) which begins at 550 °C and ends in the vicinity of 1000 °C. This mass loss probably corresponds to the removal of the hydroxyl groups. The total weight loss is approximately 68% of the initial mass of the precursor at 1000°C.

On DSC curves during heating, phase changes cause absorption or release of heat, which manifests as an endothermic (exothermic) peak during the reaction. The DSC analysis curve (fig.3.b) shows the existence of several peaks:

- A large peak at 110 °C corresponding to the evaporation of water
- Two exothermic peaks at 417 and 655 °C, the first can be attributed to the formation of aluminum and zinc hydroxide phases, and the second broad peak is due to the formation of the cubic structure spinel ZnAl$_2$O$_4$. We have also noticed that the increase in the quantities of Pb leads to the small displacement of the peaks towards the low temperatures.

### 3.4 Raman analysis

It is well known that Raman spectroscopy is a characterization method to measure the frequencies of the long-wavelength lattice vibrations (phonons). Raman spectroscopy provides a fast and convenient method for detecting small structural changes in materials. On the other hand, according to group theory, ZnAl$_2$O$_4$ should exhibit five Raman active modes: $A_{1g} + E_g + 3T_{2g}$ [38]. However, the figure 4 displays Raman spectra of all samples treated at 900°C for 2h. These spectra are similar and reveal the presence of four peaks located at 196, 419, 512 and 660 cm$^{-1}$ and correspond, respectively, to $T_{2g}$, $E_g$, $T_{2g}$, , and $T_{2g}$ phonon frequencies of ZnAl$_2$O$_4$ spinel structure [20,38-40]. In addition, peak $T_{2g}$ (3) at 660 cm$^{-1}$ is most intense and represents the fingerprint of ZnAl$_2$O$_4$ spinel [17]. Obviously, the peak located at 727 cm$^{-1}$ corresponding to the active mode $A_{1g}$ is not observed on our spectra. This peak is attributed to the symmetrical stretching vibration Al-O of the AlO$_4$ groups created by the redistribution of certain aluminium ions from the octahedral sites to the tetrahedral sites [41]. Therefore, the ZnAl$_2$O$_4$ spinel formed in our samples shows very little inversion. Furthermore, the $E_g$ peak at 419 cm$^{-1}$ also does not show the asymmetry typical of disordered ZnAl$_2$O$_4$ spinel as shown in figure 5 [38]. We can conclude that the results obtained by Raman spectroscopy confirm those found by X-ray diffraction.
3.5 UV-VIS

The diffuse reflectance spectra of the samples annealed at 900 °C for 2h in a range of 240 to 800 nm are presented in figure 6. For all the samples, we observed an absorption band in the UV (220-270 nm) region, which can be attributed to the band-to-band transition of the AlO6 in ZnAl2O4 spinel [42-43]. Another absorption band appears at 460 nm for the S0 sample and which shifts towards low wavelengths up to 1% mol Pb²⁺, then it takes the reverse path up to 350 nm (S4 sample), to finally disappear giving a wide band for sample S5. This band arises from the defects absorption within the spinel material. Also, we notice that the absorption edge shifts slightly towards the low energies, with increase of % Pb²⁺ doping. However, in the VIS region from 450 to 720 nm, the reflectance improves with the increase of the doping (% mol Pb²⁺). The maximum reflectance is obtained for 1% mol La³⁺ and 0% Pb²⁺ (S0 sample). We note, that this improvement of reflectance has been observed also in Sm (0.5% mol): ZnAl2O4 nanomaterials synthesized by vibrational milling [11].

The band gap energy (Eg) of the ZnAl2O4 samples can be determined from plots of (K hv)ⁿ versus hv shown in figure 7 (with n = 2, which is appropriate for a direct band gap material such as ZnAl2O4) using the Tauc relation given in Equation (4)

(K hv)² = C (hv - Eg)  

(4)

Where K is the Kubelka-Munk function [35] given in equation (5):

K=(1-R)²/(2R) =F(R)  

(5)

R is reflectance (%), hv is the photon energy, C is a proportionality constant, and Eg band gap energy. The determination the intercept on the hv axis by extrapolating the linear part of the plot to (K x hv)² = 0 as shown in figure 7, give the band gap energy (Eg). The values of the obtained optical band gaps are: 3.95; 3.85; 3.70; 3.60; 3.48; 3.34 and 3.05 eV for pure ZnAl2O4, S0, S1, S2, S3, S4 and S5 samples respectively. These results confirm the displacement of the absorption edge towards large wavelengths with the increase of the % Pb as well as the change of the forbidden band of ZnAl2O4 doped with Pb²⁺.
3.6 Scanning electron microscopy

The observations of this micrograph allow us to say that the morphology of the grains is irregular (fig.8). It varies from a spheroid shape for small particles to an elongated shape for large particles. The particle size is widely distributed with an average size of around 100 nm. This leads to the conclusion that the crystallites tend to agglomerate in small clusters [44], giving nanoparticles having sizes much larger than those of the crystallites (25 nm) calculated from Sherrer’s formula.

3.7 EDX

Figure 9, showing the spectrum of pure ZnAl$_2$O$_4$, clearly indicates the detection of the elements (Zn, Al, and O) present in pure zinc titanate. While in fig. 9.b, which represents the spectrum of sample S1, we note, in addition to the matrix elements, the presence of dual doping elements (La and Pb) [45]. We also observe on the other spectra which are not represented here, that the intensity of the lead peak increases when the percentage of the latter increases. The presence of carbon comes from the metallization of the samples.

3.8 Photocatalytic activity

As shown in Fig. 10, the degradation of HCV by direct photolysis requires which may appear in practice too long; this renders the process of little benefit to environmental applications as compared to other methods. For this reason, we examined: (i) adsorption and (ii) photo catalysis. Experimentally, the only difference between the two processes is the absence and presence of ultraviolet radiation in adsorption and photocatalysts respectively.

Figure 11 (a), (b) and (c) compares the results obtained with those of direct photolysis, it is clear that the addition of ZnAl$_2$O$_4$ powder of different types in the reaction medium considerably accelerates the degradation of the dye. Besides to that the dispersion rate is different compared to the powder used.

Before UV-light irradiation, each suspension of photocatalysts/HCV solutions was continuously stirred in the dark for 30 min to reach an adsorption-desorption equilibrium. For the entire sample, the adsorption efficiency of HCV varied between 0 and 30%, 45% and 55% in ZnAl$_2$O$_4$-ZnO, pure ZnAl$_2$O$_4$ and S5 respectively. These
results indicate that the synthesized ZnAl$_2$O$_4$ is good adsorbent, what encouraged us to continue the study of adsorption.

After 120 min of irradiation, the dye degrades by 75%, 70% and 57% by (ZnAl$_2$O$_4$ + ZnO), S5 and pure ZnAl$_2$O$_4$, respectively. The difference in dye removal rate depends on the body used. Pure ZnAl$_2$O$_4$ is the least efficient catalyst. However, the presence of Pb and ZnO respectively, in the other two samples S5 and (ZnAl$_2$O$_4$ + ZnO), makes them more potent. This is due to the fact that the atoms of lead replace the atoms of Zn and Al, which creates surface exchanges and an increase in the lattice parameter as well as a decrease in gap energy (~ 3 eV), making sample S5 more powerful and efficient than pure ZnAl$_2$O$_4$ (Eg = 3.9 eV). As for (ZnAl$_2$O$_4$ + ZnO), it is the most efficient because of its structure, its wide band gap (3 eV) and its excitonic energy of 60 meV; the highest value of all semiconductors [46]. In this study, we observe that the photocatalytic behavior of zinc aluminates strongly depends on the energy of the forbidden band (Eg) [47].

3.8.1 Discussion photocatalytic Activity

The photon excitation of ZnAl$_2$O$_4$ amounts to creating electron-hole pairs, that is, a redox system, by passing the electrons (e$^-$) from the valence band (BV) to the conduction band (BC) creating a positive hole (h$^+$) in BV.

The created holes move to the surface of the material where their high oxidizing power manifests itself towards the adsorbed oxidizable species. While the electrons produced act on the reducible adsorbed species. It is accepted that in an aerated environment, the electrons, which have acquired the energy of the conduction band, are captured by the adsorbed oxygen to give superoxide radical ions and a new state of equilibrium being established on the oxide surface [48- 50]. In our case, the electron donors can be H$_2$O, OH$^-$ or the pollutant HCV.

The mechanism of photo catalysis includes the following reactions:

\[
\begin{align*}
\text{ZnAl}_2\text{O}_4 (\text{ZnO}) + h\nu & \rightarrow \text{ZnAl}_2\text{O}_4 (\text{ZnO}) + h^+ + e^- \\
\text{H}_2\text{O} + h^+ & \rightarrow \cdot\text{OH} + \text{H}^+ \\
\cdot\text{OH} + h^+ & \rightarrow \cdot\text{OH} \\
\text{O}_2 + e^- & \rightarrow \text{O}_2^{2-} \\
\text{HCV (P)} + \cdot\text{OH} (\text{O}_2^{2-}) & \rightarrow \text{H}_2\text{O} + \text{CO}_2
\end{align*}
\]
3.9 Adsorption Activity

When the three solutions are stirred in the dark for 30 minutes, the three samples studied prefer adsorption to photo-catalysis. Figure 11. (d) indicates the monitoring of adsorption as a function of contact time (under the same conditions as photocatalysis (temperature, concentration, etc.)), allows to conclude on the one hand that the adsorption is remarkable for three samples and on the other hand that the retention rate is 50, 42 and 25% on S5, pure ZnAl₂O₄ and ZnAl₂O₄ + ZnO after 30 minutes, respectively.

After 150 minutes of contact, the remaining amount of HCV decreases and the adsorbed amount increases, the dispersion rate was found to be 64%, 60% and 50% in the presence of ZnAl₂O₄+ZnO, S5 and pure ZnAl₂O₄ respectively.

In the case of pure and doped ZnAl₂O₄, the curves have two important parts, between [0.30mn] the curve is linear, there is a rapid degradation with a high speed and more important for S5. After 30 minutes of contact, the degradation decreases with a slow and constant speed, and the curves have a flat level.

This is explained by the rapid fixation of the molecules in the first moments, because in addition to the presence of surface pores, there is a great affinity between the molecules of the dye and of the adsorbent. The formation of the kinetic plateau (C / C0) informs us that all the pores are occupied by molecules of HCV.

Concerning the ZnAl₂O₄ + ZnO sample, the adsorption is slow because from the first moments of contact up to 150 minutes, the HCV molecules slowly bind to the surface because there is a lack of affinity between ZnO and HCV molecules. On the other hand, the same isothermal model of Langmuir confirms this adsorption.

We found that the binding rate of HCV molecules is higher for the samples of S5 and pure ZnAl₂O₄ than for the sample ZnAl₂O₄ + ZnO. The affinity between the adsorbate and the adsorbent and the adsorbents structures strongly influence the binding performance, i.e. the speed fixation of the HCV molecules. in addition, doping with divalent or trivalent ions at the aluminum site can modify the structure of spinel aluminates [51]. Polarization in spinel aluminates is determined by the trivalent aluminum ion at the octahedral site [52 - 55].
4. Conclusion

The ZnAl$_2$O$_4$: 1% La$^{3+}$, x% Pb$^{2+}$ powders was successfully prepared by citrate sol-gel technique. The Raman and DRX results confirmed that all samples prepared are consisted of single-phase cubic spinel structure without other impurity phases; in addition the formation of spinel that verified through TGA/DTA analysis. Moreover, the FTIR results confirmed the presence of absorption bands from stretching and bending vibration modes of octahedral bonds (AlO$_6$) which correspond to a formation of normal ZnAl$_2$O$_4$. Meanwhile, the average value of crystallite size decrease with the increase of Pb$^{2+}$ doping up to 1% mol (19nm), and then it increases to reach 25nm at 2.5% mol Pb$^{2+}$. Regarding the lattice parameter, we notice that the Vegard’s law is violated up to 1.5% mol Pb$^{2+}$, i.e. the lattice parameter decreases instead of increasing. On the other hand, UV-Visible spectra indicate that the band gap of the dual doped samples decreased with the increase of Pb$^{2+}$ content ion concentration. Meanwhile, reflectance spectra revealed that absorption edge of ZnAl$_2$O$_4$ powders had shifted to lower energy by the addition of Pb$^{2+}$ content. From the previous results, the presence of the elementary composition for all samples was confirmed through the EDX analysis. Finally, photocatalytic study for different samples of ZnAl$_2$O$_4$ shows that they can be used like as photocatalysts and good adsorbents for degradation of Hexamethyl crystallized violet dye in aqueous solution.

Acknowledgements

We, the authors, thank the Autonoma University Spanish Laboratory, especially doctor M.Mansosilvan, for providing all the facilities required to conduct experiments in very good conditions.
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