Preparation and Characterization of Novel Zinc Aluminate Nano-Powders Doped with Copper (II), Loaded and Non-loaded with Carbon Spheres Using Co-Precipitation Method and Its Environmental Application

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Abstract

Due to rapid industrialization, the presence of heavy metals in water and wastewater is a matter of environmental concern. Though some of the metals are essential for our system but if present beyond their threshold limit value (TLV), they are harmful and their treatment prior to disposal becomes inevitable. The present communication has been addressed for the removal of Cr (VI) from aqueous solutions by synthesized zinc aluminate novel nano-materials doped with copper (II); loaded and non-loaded with carbon spheres (CSs) using the co-precipitation technology. The as-prepared precursors of Cu(x)Zn(1-x)Al₂O₄ were annealed at 1000 °C for 2 h. The characterization of the samples nanoparticles were implemented by X-ray fluorescence (XRF), X-ray diffraction (XRD), transmission electron microscopy (TEM) analysis, photoluminescence spectra (PL) as well as the optical properties was demonstrated by UV–visible–near IR spectrophotometer. The optical properties of the prepared nano-materials and their catalytic performances are well discussed. Batch experiments were adopted for the adsorption of Cr (VI) from its solutions. The effect of doped copper ions and Cu (II) / CSs co-dopants on the behavior of ZnAl₂O₄ on removal of chromium was studied using inductively coupled plasma (ICP) analysis that had been used to measure removed and remaining Cr (VI) from its water polluted samples.

Key Words: Zinc Aluminate, copper (II) and Cu (II)/CSs co-dopants, Co-precipitation, XRF, XRD, TEM, Photoluminescence (PL), Cr (VI) removal.

1.Introduction

Transition metal-oxide spinels are important in many application fields because of their high chemical and thermal stability, high mechanical resistance, hydrophobicity, and low surface acidity (Zawadzki M. 2001, Wrzyszcz J. 2002 and Nilsson M. 2009) [1-3]. They are being suitable for a wide range of applications, such as optical coating or host matrix, high temperature ceramic material, catalyst and catalyst support (Tzing WS. 1996, Phani AR 2001 and Zawadzki M. 2001) [4-6]. Among the most interesting materials of that kind, zinc aluminate (ZnAl₂O₄), with spinel structure belonging to Fd3m space group, offers many advantages. ZnAl₂O₄ is one of the best wide band gap compound semiconductor (Eg = 3.8 eV) (Chen XY. 2011)[7] for various optoelectronic applications (Li X. 2011)[8] and electronic and optical materials. Zinc aluminates were used also in photo-electronic devices, electroluminescence displays, stress imaging devices, and highly efficient phosphors. In recent years, ZnAl₂O₄ spinel has been largely used as catalyst in several reactions such as degradation of gaseous toluene (Galetti AE. 2010) [9], ethanol steam reforming (Lenarda M. 2007) [10], combustion of soot under NOx/O2 atmosphere (Zawadzki M. 2009)
[11], isobutane combustion (Staszak W. 2010) [12], and the transesterification (Pugnet V. 2010) [13] of waste frying oil (WFO) with methanol and ethanol was studied in a batch reactor using a zinc aluminate catalyst, prepared by the combustion reaction method. The reaction runs were carried out for 2 hours, using alcohol: oil molar ratio of 40:1, temperature range of 60–200 °C, catalyst ratio of 1–10% wt., using 700 rpm stirring. Spinel ZnAl₂O₄ semiconductors have been synthesized using a variety of different methods, such as the solid-state reaction method (Zou, L. 2006 and Van der Laag 2004) [14, 15] and a self-generated template pathway (Zou, L. 2006) [14], the combustion method (Ianos, R. 2012) [16], the sol–gel method (Wei X. 2006) [17] and a co-precipitation approach (Cheng B. C. 2013) [18], were also employed. The polymeric precursor method (Gama L. 2009) [19], the citrate precursor method (Li X. 2011) [20], a hydrothermal process (Zhu, Z. R. 2012) [21], a solvent-thermal approach (Fan G. L 2011) [22], and the microwave-hydrothermal route (Zawadzki M. 2009) [11] had been employed. Several doped ZnAl₂O₄ compounds, were described how the materials properties can be improved according to the dopants or the doping methods as explained in previously published research papers [23-27]. The present paper, Cu₀.₅Zn₁₋₀.₅Al₂O₄ nanoparticles have been synthesized by co-precipitation where x (0.2, 0.4, 0.6, 0.8 and 1.0). Then loaded the prepared nanoparticles with CSs. Cu₀.₅Zn₁₋₀.₅Al₂O₄ nanoparticles loaded and non-loaded with CSs were investigated to check the change in phase structure and crystallite sizes of the newly prepared spinels. Also their optical properties and their behavior toward the removal of Cr (VI) from its polluted sample solutions were studied.

2. Experimental

2.1. Materials:
The chemicals used in this research are of the analytical grade. They included aluminum chloride hexahydrate (AlCl₃.6H₂O 98%, 241.45 g mol⁻¹, Loba, Chemie). Zinc chloride (ZnCl₂ 97%, 136.286 g mol⁻¹ Loba Chemie) and copper chloride (CuCl₂ 98%, BDH chemical Ltd.). They also included sucrose (C₁₂H₂₂O₁₁ 99.5%, 342.30 g mol⁻¹, Sigma-Aldrich) as a source of carbon spheres, ammonium carbonate ((NH₄)₂CO₃ 99.9%, 96.09 g mol⁻¹, Sigma-Aldrich) as a reagent and potassium dichromate (K₂Cr₂O₇ 99.0%, 294.18 g mol⁻¹, Sigma-Aldrich) as a source of hexavalent chromium. Hydrochloric acid (HCl) (M.wt = 36.46 g mol⁻¹) with purity 30-34 % was purchased from ADWIC. The distilled water used in all preparations usually collected from all glass equipment.

2.2. Solutions
A solution of 0.1 M Zinc chloride ZnCl₂ (> 97% purity) (M.wt = 136.286 g mol⁻¹), was prepared by dissolving the accurately weighed amount (1.36286g) in least amount of HCl (~1 ml) and the volume completed with distilled water to 100 mL in volumetric flask.
A solution of 0.1 M aluminum chloride hexahydrate AlCl₃.6H₂O (> 98%) (M.wt = 241.45 g mol⁻¹), was prepared by dissolving the accurately weighed amount (2.4145 g) in the appropriate volume of distilled water and the volume completed to 100 mL volumetric flask.
A solution of 2000 ppm from potassium dichromate was prepared by dissolving the accurately weighed amount (0.5g) in appropriate volume and then completed with distilled water in 250 mL volumetric flask.

2.3. Preparation Procedures for Nano-spinels

2.3.1. Synthesis of carbon spheres
Carbon spheres (CSs) were prepared by one step process, where sucrose is the source of carbon then heated at 100oC for 24h.

2.3.2. Synthesis of zinc aluminate doped with Cu(II) nanoparticles using co-precipitation method non-loaded with carbon spheres
Zinc aluminate doped with copper ion was synthesized, by inserting the aqueous solution of zinc chloride (ZnCl₂ 97%) into aqueous solution of aluminum chloride hexahydrate (AlCl₃.6H₂O 98%), no further purification, with molar ratios 1: 2 of Zn: Al. Then the previous mixture was mixed with aqueous solution of copper chloride (CuCl₂ 98%); which has molar ratios of 0.0, 0.2, 0.6, 0.8, and 1.0. Afterwards, ammonium carbonate solution added drop-wisely into the mixture with stirring under strong ultrasonic agitation until pH of the solution reached 7. The powder was filtered, washed with deionized water, and dried at 100 °C overnight.

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Table 1 The theoretical and practical weight percentage of elements in Cu$_{x}$Zn$_{1-x}$Al$_2$O$_4$ nano-powder non-loaded with carbon spheres (CSs) doped with Cu (II) of $x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$ using co-precipitation method and using XRF.

<table>
<thead>
<tr>
<th>$\text{Cu(II)}$ ions molar ratio</th>
<th>Practical weight percentage (%)</th>
<th>Theoretical weight percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(II)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>34.65</td>
<td>36.00</td>
</tr>
<tr>
<td>0.2</td>
<td>28.00</td>
<td>28.85</td>
</tr>
<tr>
<td>0.4</td>
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</tr>
<tr>
<td>0.6</td>
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<td>14.35</td>
</tr>
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<td>9.00</td>
<td>7.19</td>
</tr>
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<td>1.0</td>
<td>0.01</td>
<td>0.00</td>
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<tr>
<td>Cu(II)</td>
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<td></td>
</tr>
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<td>0.14</td>
<td>0.00</td>
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<td>8.00</td>
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<td>34.77</td>
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<tr>
<td>1.0</td>
<td>33.58</td>
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</tr>
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</table>

Table 2 The XRF determined weight taken percentage and weight found of carbon spheres used for loading with zinc aluminate doped with Cu(II) nanoparticles synthesized by co-precipitation method.

<table>
<thead>
<tr>
<th>$\text{Cu(II)}$ ions molar ratio</th>
<th>Weight taken percentage (%) of CSs</th>
<th>Weight found percentage (%) of CSs</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>25.00</td>
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</tr>
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<td>0.2</td>
<td>25.00</td>
<td>24.22</td>
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<td>23.40</td>
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<tr>
<td>0.6</td>
<td>25.00</td>
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2.3.3. Synthesis of zinc aluminate doped with Cu(II) nanoparticles using co-precipitation method loaded with carbon spheres

The prepared Cu$_{x}$Zn$_{1-x}$Al$_2$O$_4$ nano-powder ($x=0.0, 0.2, 0.4, 0.6, 0.8, 1.0$) from 2.3.2 were be added to carbon spheres, by grinding CSs with Zn$_{1-x}$Al$_2$O$_4$ nano-powders ($x=0.0, 0.2, 0.4, 0.6, 0.8, 1.0$) in proportions 25% of CSs and 75% of Zinc aluminate doped with Cu(II) nanoparticles for 20 min.

2.4. Structure studies of the prepared nano-materials

2.4.1. X-ray fluorescence (XRF) study

The X-ray fluorescence (XRF) is a powerful quantitative and qualitative analytical tool for elemental analysis of materials. Determination of the elements were carried out using X-ray fluorescence spectroscopy (XMDS 2726), with max.45 KV/ 50 μA.

2.4.2. The X-Ray Diffraction (XRD) study

XRD patterns of the resulting nano-powders were characterized by a Brucker D8-advance X-ray powder diffractometer CU Kα a radiation (k ¼ 1.5406 Å). The crystallite sizes of the produced zinc aluminate spinels were calculated from the most intense peak using Debye Scherrer formula:

\[
d_{K\beta} = \frac{k \lambda}{\beta \cos 2\theta}
\]

Where \( d_{K\beta} \) is the crystallite size, \( k = 0.9 \) is a correction factor to account for particle shapes, \( \beta \) is full width at half maximum (FWHM) of the most intense diffraction peak (3 1 1) plane, \( \lambda \) is the wavelength of Cu target = 1.5406 Å, and \( \theta \) is the Bragg angle at \( 2\theta = 35.42^\circ \) which is strongest peak was used to calculate the average size of the nanoparticles.

2.4.3. Morphology studies of the prepared spinels

The micrographs of produced Cu$_{x}$Zn$_{1-x}$Al$_2$O$_4$ spinel samples were inspected by direct observation via high resolution transmission electron microscope (HR TEM; JEM-2100, Japan). HR-TEM samples were prepared by dispersing the powders in acetone. Ultrasonic oscillation for 1 h was introduced to decrease the aggregation followed by placing a drop of the suspension on holey carbon film supported on copper grids.

2.4.4. Spectral measurements

The UV-VIS absorption and diffuse reflectance spectrum of the prepared nano-materials were recorded at room temperature using UV-VIS-NIR spectrophotometer (Jasco-V-570 spectrophotometer, Japan) fitted with integrating sphere reflectance unit (ISN) in the wavelength range 200-2000 nm. Photoluminescence (PL) spectra were obtained at room temperature using fluorescence spectrophotometer (SHIMADZU RF-5301PC Japan) with xenon discharge lamp (150 W) as excitation source, at room temperature using an excitation wavelength equal to 200 nm.

2.5. Environmental application of the prepared nano-spinels

2.5.1. Adsorption procedure:

Removal of Cr(VI) from aqueous solutions of concentration 2000 ppm for 1 h in contact with 1 g nano-material samples during constant stirring. The amount of the adsorbed cation is obtained by difference of Cr (VI) concentration before and after adsorption by using ICP-AES. The percent removal = [Cr VI] after/ [Cr VI] before X 100.

2.5.2. Measurements:

To study, detect and measure removal of Cr (VI) from wastewater were inspected by inductively coupled plasma (ICP) with torch has a diameter 0.5-1.0 inch and magnetic field oscillates at 27.2 MHz typically argon gas is the plasma gas and nebulizer gas (with the sample) the formed plasma contains a high properties of cations and electrons and has electron density 10$^{13}$-10$^{15}$ electrons/cm$^3$.

3. Results and discussion

Before going to investigate structure of the newly prepared nano-materials by co-precipitation method, the proposed general formulae (Cu$_{x}$Zn$_{1-x}$Al$_2$O$_4$) of these compounds should be proved by elemental analysis (EL) of its element constituents like Zn and Al together with the dopants Cu and Cu/CSs. Due to the insolubility of the prepared nan-powders; the used of X-Ray Fluorescence (XRF) is strongly recommended.

3.1. Elemental Analyses (EA) by X-Ray Fluorescence (XRF)

The calculated theoretical and practical weight percent’s of constituent elements of the novel prepared Cu(x)Zn(1-x)Al$_2$O$_4$ nano-powder had been determined by XRF at different ratios of doped copper ($x=0.0, 0.2, 0.4, 0.6, 0.8, 1.0$) and/or doped CSs are given in Tables (1 and 2)
3.1.1. XRF of zinc aluminate substituted by Cu(II) nanoparticles synthesized by co-precipitation method non-loaded with carbon sphere

From the data presented in Table 1, it is clear that the calculated weight percent of the elements and practical found percent are correlated to each other; which means that the formed nanoparticles have similar proportions without any contaminations. These data confirm the proposed general formulae of the newly prepared zinc aluminate doped with Cu(II); Cu(x)Zn(1-x)Al2O4 nano-powder at different ratios x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0 and proved its correct proportions.

3.1.2. XRF determined carbon spheres used for loading zinc aluminate doped with Cu(II) nanoparticles and synthesized by co-precipitation method

The data presented in Table 2 refer to a good correlation between theoretical and practical data of CSs%; and found to be close to 25%, so the proportions of CSs and zinc aluminate doped with Cu (II) nanoparticles are closely 25% to 75% respectively. These data also confirm the successful insertion of carbon spheres in the entity of the prepared nanomaterials obtained by co-precipitation technique at different doped Cu(II) ratios.

3.2. XRD used for identification of structural formulae of zinc aluminate nanoparticles doped with Cu (II) and/or with carbon spheres (CSs) using different techniques:

3.2.1. X-ray diffraction analysis of carbon spheres (CSs) non-loaded zinc aluminate

Table 3: Variation of crystallite size, Bragg angle, lattice parameter, unite cell volume and X-ray theoretical density of Cu(x)Zn(1-x)Al2O4 where x 0.0, 0.2, 0.4, 0.6, 0.8, 1.0 molar ratios annealed at 1000 °C for 2 h using co-precipitation method non-loaded with CSs

<table>
<thead>
<tr>
<th>Cu(II) ions molar ratio</th>
<th>Cry. Size (nm)</th>
<th>Bragg angle (2θ)</th>
<th>Lattice parameter (Å)</th>
<th>Unite volume (Å³)</th>
<th>Cell volume (g/cm³)</th>
<th>X-ray theoretical density (g/cm³)</th>
<th>Optical band gap energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>23.4</td>
<td>36.957</td>
<td>8.0606</td>
<td>523.7220</td>
<td>4.6507</td>
<td>3.58</td>
<td>3.58</td>
</tr>
<tr>
<td>0.2</td>
<td>25.2</td>
<td>36.954</td>
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<td>4.6556</td>
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<td>2.28</td>
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<tr>
<td>0.4</td>
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<td>8.0740</td>
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<td>522.0366</td>
<td>4.6189</td>
<td>2.02</td>
<td>2.02</td>
</tr>
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</table>

Fig 1: XRD patterns of Cu(x)Zn(1-x)Al2O4 (x from 0.0 to 1.0 molar ratios) annealed at 1000 °C for 2 h using co-precipitation
Fig. 1 shows the XRD diffraction profiles of Cu ion doped in Cu_{x}Zn_{1-x} Al_{2}O_{4} (x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0 molar ratios) synthesized by co-precipitation method. It can be seen that the prepared nano-materials are present in single phase. The peaks are belonging to cubic structure with space group Fd-3m (JCPDS card # 74-1136) for ZnAl_{2}O_{4} phase and (JCPDS card # 78-1605) for CuAl_{2}O_{4}. Also the figure shows that right shift after increasing copper percentage.

In Table 3 the crystallite size of zinc aluminate doped with cupper by using co-precipitation method show a slightly change in their values due to the similarity in properties between copper and zinc. The lattice parameter “a” of the samples was calculated using the following equation

\[ d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}} \]  

(2)

Where \( a \) is the lattice parameter, \( d \) is the inter-planar distance and \( (hkl) \) are the Miller indices. The values of lattice parameter and unit cell volume are listed in Table 3. The X-ray theoretical density was estimated using the following equation

\[ \rho_X = \frac{\sum A}{N_{AV} V} \]  

(3)

Where \( \rho_X \) is the X-ray theoretical density, \( A \) is sum of the atomic weights of all the atoms in the unit cell, \( V \) is the volume of the unit cell and \( N_{AV} \) is the Avogadro’s number. It can be seen that the lattice parameter \( (a) \) and unit cell volume were slightly changed by addition of copper to zinc aluminate.

3.2.2. XRD of Zinc aluminate doped with Cu(II) Nano-particles loaded with carbon spheres (CSs) synthesized by co-precipitation method

XRD diffraction profiles of Cu_{x}Zn_{1-x} Al_{2}O_{4} (x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0 molar ratios) synthesized by co-precipitation method loaded with carbon spheres shown in Table 4 and in Fig.2.

<table>
<thead>
<tr>
<th>Cu(II) molar ratio</th>
<th>Cry. Size (nm)</th>
<th>Optical band gap energy (eV)</th>
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</thead>
<tbody>
<tr>
<td>0.0</td>
<td>15.09</td>
<td>2.55</td>
</tr>
<tr>
<td>0.2</td>
<td>17.21</td>
<td>2.19</td>
</tr>
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<td>17.88</td>
<td>1.83</td>
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</table>

3.3. Morphology and microstructure

The morphology of the prepared nano-materials had been studied by Field Emission Scanning Electron
Microscope (FE-SEM) and High Resolution Transmission Electron Microscopy (HRTEM).

3.3.1. Field emission scanning electron microscopy (FE-SEM)
The morphology of the synthesized carbon spheres was investigated by FE-SEM and the results are shown in Fig.3.

3.3.2. High Resolution Transmission Electron Microscopy (HR-TEM)
The morphology of the prepared nano-material both loaded and non-loaded with carbon spheres (CSs) had been carefully investigated by the most efficient technology (HR-TEM). The results obtained are shown in Figs (4 and 5).

3.3.2.1. HR-TEM of zinc aluminate doped with Cu(II) nanoparticles non-loaded with carbon spheres synthesized by co-precipitation method
The morphology of zinc aluminate doped with Cu(II) nanoparticles non-loaded with carbon spheres synthesized by co-precipitation method is found to be homogeneous and spinel particles with cubic structure consist of uniform quasi-spherical crystallites of an average size ~ 25 nm in Fig.(4.a) for pure zinc aluminate. After doping with copper ions Fig.(4.b), Cu(II) inter to the lattice of zinc aluminate and form a new shell so the interspace and aggregation increase with copper and form a regular and uniform shape. Aluminum and copper agglomerated well which found in pure copper aluminates Fig.(4.c). The particle sizes of the prepared samples shown via HR-TEM are very close to the detected values obtained from the XRD measurements.

![Fig.3 FESEM micrographs of carbon sphere](image)

The results in Fig.3 certify that the carbon spheres have a spherical morphology (Zhuang Z.-H. 2009) [28] with good dispersed structure and highly homogeneous in size. The figure shows that the sizes of the carbon spheres ~ 60 nm; so when carbon spheres added to the nanoparticle (zinc aluminate substituted with copper ion) will form a nano-composite of good homogeneity.

3.3.2.1. HR-TEM of zinc aluminate doped with Cu(II) nanoparticles loaded with carbon spheres synthesized by co-precipitation method
The HR-TEM micrographs of Cu_{x}Zn_{(1-x)}Al_{2}O_{4} (x=0.0, 1.0) loaded with carbon spheres are shown in Fig.(5.a, b).

![Fig.4 HR-TEM micrographs for Cu_{x}Zn_{(1-x)}Al_{2}O_{4} where a) x is 0.0, b) x is 0.6 molar ratios and c) x is 1.0 molar ratio annealed at 1000°C for 2 h using co-precipitation method not loaded with carbon spheres](image)

Fig. 4 results show that; the morphology is homogeneous and spinel particles with cubic structure consist of a spherical crystallites of an average size ~ 15 nm in Fig.(5.a) for pure zinc aluminates.
aluminate which is very small and copper aluminate has a crystal size ~ 18 nm Fig.(5.b), which equivalent to XRD data. These micrographs give an indication that there is a great combination between CSs and spinal moiety; which cause the decreasing in the crystal size.

3.4. Optical properties
Among the most interesting materials of that kind, zinc aluminate (ZnAl$_2$O$_4$), with spinel structure belonging toFd3m space group , offers many advantages. ZnAl$_2$O$_4$ is one of the best wide band gap compound semiconductor (Eg = 3.8 eV) (Chen XY. 2011)[7] for various optoelectronic applications (Li X. 2011)[8] and electronic and optical materials. Zinc aluminates were used also in photo-electronic devices, electroluminescence displays, stress imaging devices, and highly efficient phosphors. Consequently the study of optical properties and semiconducting ability of the newly prepared Zinc aluminate doped with Cu (II) and co-doped with Cu (II)/CSs via energy gap calculation from their optical properties is very important to confirm its possible practical applications. The applied techniques are UV-VIS-NIR and photoluminescence spectroscopy (PL).

4.2.1. UV-VIS-NIR Spectra of zinc aluminate doped with Cu(II) nanoparticles synthesized by co-precipitation method and non-loaded with carbon spheres

UV-VIS-NIR Spectra of zinc aluminate doped with Cu(II) nanoparticles synthesized by co-precipitation method non-loaded with carbon spheres are shown in Figs.6 and 7.

![Fig.6: (a) Absorbance (b) Reflectance of Cu$_x$Zn$_{1-x}$Al$_2$O$_4$, nano-powders (where x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0) using co-precipitation method non-loaded with CSs](image)

The results of the recorded absorbance (A) revealed characteristic peaks of Al and Cu ions. The absorbance of 35% of pure zinc aluminate increases with increasing copper ratios until it reaches 85% in case of pure copper aluminate at x = 1.0 (Fig.6). From these results energy gap (Eg) in the structures of these nano-materials the absorption (A) is converted to the absorption coefficient (α) using the following relation.

$$\alpha(\nu) = \frac{1}{d} \ln \left(\frac{I_0}{I}\right) = \frac{(100-R)}{2R}$$  (4)

Where ln (Io/I) is the absorbance (A) and d is the thickness of the sample. The reflectivity R can be transformed into a value proportional to the absorption using the Kubelka–Munk function:

$$(h\nu F(Rx))^n = A (h\nu - E_g)$$  (5)

The obtained results of the calculated band gap energy are represented in Fig.7; of the prepared Cu$_x$Zn$_{1-x}$Al$_2$O$_4$ (where x= 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) spinel nanoparticles without carbon spheres was estimated by extrapolating the linear portion of Tauc’s plot to $(h\nu F(Rx))^n$ versus photon energy $(h\nu)$ (n=2, for a direct band gap material). The optical band gap energy values (Table 3) are reduced from 3.58 eV for pure ZnAl$_2$O$_4$ to 2.02 for pure CuAl$_2$O$_4$ by increasing the molar ratio x = 0.0 to 1.0 of Cu(II).

4.1. UV-VIS-NIR Spectra of zinc aluminate doped with Cu(II) nanoparticles synthesized by co-precipitation method loaded with carbon spheres

![Fig.7: Optical energy gap of Cu$_x$Zn$_{1-x}$Al$_2$O$_4$, nano-powders (where x = 0.0 to 1.0) by using co-precipitation method non-loaded with CSs](image)
The results obtained of UV-VIS-NIR Spectra of Cu(x)Zn(1-x)Al2O4 (x =0, 0.2, 0.4, 0.6, 0.8 and 1.0) loaded with carbon spheres are shown in Figs.8 and 9.

Fig.8. (a) Absorbance (b) Reflectance of Cu(x)Zn(1-x)Al2O4 nano-powders (where x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0) using co-precipitation method loaded with carbon spheres

These results revealed that; after binding Cu(x)Zn(1-x)Al2O4 (x =0, 0.2, 0.4, 0.6, 0.8 and 1.0) loaded with carbon sphere, there is an increase in the absorbance of pure zinc aluminate from 35% to 68%; which related to carbon sphere, however the absorbance of pure copper aluminate is still 85% (Fig.8a). These results are used for calculation of energy gap values (Eg) according to equations (4) and (5) and graphically represented in Fig. 9. These results revealed that; there is a noticeable change in the band gap of Cu(x)Zn(1-x)Al2O4 (x =0, 0.2, 0.4, 0.6, 0.8 and 1.0) with variation of percent of carbon sphere. The band gap decreases from 3.58 eV to 2.55 eV for pure zinc aluminate and from 2.02 eV to 1.83 eV for pure copper aluminate (Table 4).

4.3. Photoluminescence spectroscopy (PL)

Photoluminescence (PL) spectroscopy is a useful tool to evaluate the quality and to study the physical parameters of semiconductor materials. PL spectra were recorded to investigate the recombination phenomena in the samples. PL can study the emission spectrum and provide information about the crystal defects of semiconductor; which might be due to the oxygen vacancies. Additionally, it can find the wavelength which has the maximum emission for the sample (the material which has high emission then have high absorbance at this wavelength) equation (3). Energy Equation of Quantum Mechanics from the following equation

\[ E = \frac{hc}{\lambda} \]  

Where \( h \) is Plank’s Constant, \( C \) is Speed of light and \( \lambda \) is wavelength.

So; it is possible to obtain the information of sub-band gap defect states (Kurbanov S.S. 2010) [29] in materials; which can be influenced by the synthesis condition (Anand GT. 2013) [30].

4.3.1. PL of zinc aluminate doped with Cu(II) nanoparticles synthesized by co-precipitation method and non-loaded with carbon spheres

Fig.10 represents the PL spectra of Cu(x)Zn(1-x)Al2O4 nano-powders (where x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0) non-loaded with carbon spheres are measured at room temperature recorded with 200 nm excitation wavelength.

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Fig. 10 PL of Cu_{x}Zn_{(1-x)}Al_{2}O_{4} nano-powders (where x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0) by using co-precipitation method non-loaded with CSs

In Fig.10, all samples show violet emission centered at about 400 nm (~3.10 eV) and exhibit weak broad luminescence bands with blue emission peak at 475 nm (~2.61 eV) and orange emission peak at 590-600 nm (~2.10 -2.07 eV). The emission peaks that occurred in the PL spectra of each metal aluminate samples are attributed to the recombination of electrons and photo-generated holes involving various structural defects, such as the ionized charge states of intrinsic defects, oxygen vacancies, metal (Zn, Cu) vacancy, metal interstitials, and oxygen antisites (Anand GT, 2010, than it T2019) [31, 32]. An electron in the valence band (VB) can be excited to higher energy levels in the conduction band (CB) and then falls to the conduction band maximum (CBM) through internal conversion (IC) and vibrational relaxation (VR). The electron at CBM can then radiatively recombine with a hole in the valence band or defect states in the band gap resulting in the violet, blue and orange light emissions. Therefore, the photoluminescence analysis of ZnAl_{2}O_{4} nano-powders doped Cu(II) ions with different molar ratios exhibit interesting abilities for applications in violet, blue and yellow light-emitting devices.

4.3.2. PL of zinc aluminate substituted by Cu(II) nanoparticles synthesized by co-precipitation method loaded with carbon spheres

Fig.11 shows the PL spectra of Cu_{x}Zn_{(1-x)}Al_{2}O_{4} nano-powders (where x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0) loaded with carbon spheres measured at room temperature recorded with 200 nm excitation wavelength.

Fig. 11. PL of Cu_{x}Zn_{(1-x)}Al_{2}O_{4} nano-powders (where x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0) using co-precipitation method loaded with carbon spheres

There is no change in the PL spectra data after combination with carbon spheres. Fig.11 shows violet emission centered at about 400 nm (~3.10 eV) and exhibit weak broad luminescence bands with blue emission peak at 475 nm (~2.61 eV) and orange emission peak at 590-600 nm (~2.10 -2.07 eV). Also the intensity of the peaks decreases and become boarder so photocatalytic activity increases (jing L. 2006) [33]. Generally, also it is found that, the intensity decrease after doping with Cu(II) due to the inhibition of recombination of charge carriers and inducing geometrical distortion and creation of oxygen vacancy so during doping the energy levels increase so reducing the band gap Tables 5, 6 simultaneously decrease in the recombination rate of electron-hole due to which intensity decrease and peak are boarded that means low recombination of electron and holes give better photocatalytic activity (jing L. 2006) [33].

4.4 Removal of Cr (VI) from aqueous solutions

4.4.1. Cr (VI) removal with Cu doped zinc aluminate nanoparticles non-loaded with carbon spheres

Chromium is an important strategic metal widely used in many fields due to its distinct properties (Lu D. 2017, Zadorozhnyy V.Y. 2014, Ma H. 2017, Zhao J. 2018, Xu X.-R. 2004) [34-38]. In the earth, chromium mainly exists in the oxidative states of hexavalent chromium and trivalent chromium. The chromium (III) compounds are relatively safe, stable, have low solubility and mobility. Chromium (VI) mainly exists as chromate (CrO_{4}^{2-}, HCrO_{4}^{2-}) and dichromate (Cr_{2}O_{7}^{2-}); which has high solubility. Due to hazardous contaminant (Nasseh N. 2017, Jyothi M.S. 2017) [39, 40] of chromium (VI), its removal
has attracted much more attention, such as physical methods, like adsorption (He X. 2017, Li S. 2017, Fu R. 2017, Ouyan X. 2017) [41–44], electrochemical (Zayed et al. 2020) [45], and membrane filtration (Zhao J. 2018) [40], chemical precipitation (Peng H. 2018) [46], coagulation (Lu J. 2016) [47], and chemical reduction (Zhu Y. 2018, Yin W. 2017) [48,49] are often used to remove chromium (VI). Additionally, some biological treatments (Nhät-Thien N. 2018, Wei Y. 2017) [50, 51] and phytochemical treatments (Liu T. 2010) [52] are also applied to remove chromium (VI) in waste water and groundwater. Lead sulfate as a precipitation is used to precipitate chromium (VI) and it can remove chromium (VI) from 0.2 mol/L to 0.15 mmol/L, as shown in a recent study (Peng H. 2018) [51], but lead sulfate is a second pollutant, which is harmful for the environment. Recently, Chitosan can be used as an adsorbent for removal of Hexavalent Chromium, especially at low Cr (VI) concentrations (Dandhi G. 2018) [53], and another technology was applied (Zayed et al. 2020) [54].

In the present research zinc aluminate doped with Cu(II) and co-doped with Cu (II)/CSs in different molar ratios (0.0, 0.2, 0.4, 0.6, 0.8, 1.0) and prepared by co-precipitation method are used for removal of Cr(VI) pollutant from aqueous solutions containing 2000 ppm within limited time. The obtained results are presented in Tables 5 and 6.

Table 5: Variation of chromium (VI) using Cu$_{x}$Zn$_{1-x}$O$_4$Al$_2$O$_4$ where x 0.0, 0.2, 0.4, 0.6, 0.8, 1.0 molar ratios annealed at 1000°C for 2 h using co-precipitation method non-loaded with carbon spheres (CSs).

<table>
<thead>
<tr>
<th>Cu(II) ions molar ratio</th>
<th>Cr(VI) Remained (ppm)</th>
<th>Cr(VI) Remained %</th>
<th>Cr(VI) Removed %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>960</td>
<td>48.00</td>
<td>52.00</td>
</tr>
<tr>
<td>0.2</td>
<td>795</td>
<td>39.25</td>
<td>60.25</td>
</tr>
<tr>
<td>0.4</td>
<td>650</td>
<td>32.50</td>
<td>67.50</td>
</tr>
<tr>
<td>0.6</td>
<td>525</td>
<td>26.25</td>
<td>73.75</td>
</tr>
<tr>
<td>0.8</td>
<td>350</td>
<td>17.50</td>
<td>82.50</td>
</tr>
<tr>
<td>1.0</td>
<td>285</td>
<td>14.25</td>
<td>86.75</td>
</tr>
</tbody>
</table>

From the data presented in Table 5, it is clear that after doping of zinc aluminate nanoparticles with Cu(II) and the removal of Cr (VI) increases from 52% for zinc aluminate to 86.75% for copper aluminate. The highest removal of Cr(VI) is shown for Cu$_{0.8}$Zn$_{0.2}$O$_4$Al$_2$O$_4$ (60.25 %) and Cu$_{0.0}$Zn$_{0.8}$O$_4$Al$_2$O$_4$ reaches (82.5%) and 86.75% for pure copper aluminate at x = 1.0 respectively that attributed to the behavior and properties of copper over zinc. Therefore, Cu$_{x}$Zn$_{1-x}$O$_4$Al$_2$O$_4$ nano-powders (where x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0) can be considered as an effective adsorbent to remove chromium (VI) ions from wastewater.

4.4.2. Cr (VI) removal with Cu doped zinc aluminate nanoparticles loaded carbon spheres

Table 6: Variation of chromium (VI) using Cu$_{x}$Zn$_{1-x}$O$_4$Al$_2$O$_4$ where x 0.0, 0.2, 0.4, 0.6, 0.8, 1.0 molar ratios annealed at 1000°C for 2 h using co-precipitation method loaded with carbon spheres

<table>
<thead>
<tr>
<th>Cu(II) ions molar ratio</th>
<th>Cr(VI) Remained (ppm)</th>
<th>Cr(VI) Remained %</th>
<th>Cr(VI) Removed %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>911.57</td>
<td>45.78</td>
<td>54.22</td>
</tr>
<tr>
<td>0.2</td>
<td>594.40</td>
<td>29.72</td>
<td>70.28</td>
</tr>
<tr>
<td>0.4</td>
<td>338.60</td>
<td>16.93</td>
<td>83.07</td>
</tr>
<tr>
<td>0.6</td>
<td>207.80</td>
<td>10.39</td>
<td>89.61</td>
</tr>
<tr>
<td>0.8</td>
<td>195.50</td>
<td>9.75</td>
<td>91.25</td>
</tr>
<tr>
<td>1.0</td>
<td>95.30</td>
<td>4.77</td>
<td>95.23</td>
</tr>
</tbody>
</table>

The results represented in Table 6 it is clear that, after loading carbon spheres to zinc alumimates doped with copper ion, the nanoparticles become more active and the removal of Cr(VI) increases from 54.22% for pure ZnAl$_2$O$_4$ to 91.25% for doped Cu (II)/CSs Zinc aluminate at x = 0.8 and up to 95.23 for CuAl$_2$O$_4$ doped with CSs. This means that pure Zinc aluminate doped/co-doped Cu$_{x}$Zn$_{1-x}$O$_4$Al$_2$O$_4$ and pure copper aluminate doped with CSs are highly effective in removal of Cr(VI) (95.23%) than those doped only with Cu (II) ions (86.23 %). Comparing these results with the obtained values in Table 4, it is clear that generally removal of Cr (VI) % with the prepared nanomaterials is increased in presence of CSs than without CSs; even pure Zinc aluminate doped with CSs (54.22%) and pure copper aluminate doped with CSs (95.23%).

5. Conclusions

The first part of this work is preparation of zinc aluminate doped with copper (II) of various molar ratios x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0 by co-precipitation method. By using XRF data in elemental analysis, the general formulae of the prepared nano-materials were proved via their
elemental analyses. It is proved the correct ratios of zinc aluminate constituents doped with copper and 
Cu (I)/CSs co-dopant nanoparticles are formed. By 
studying the structure and morphology of the 
nanoparticles using XRD and HR-TEM they confirm 
a single phase with a homogenous and uniform 
structure having a cubic shape of Cu<sub>x</sub>Zn<sub>1-x</sub>Al<sub>2</sub>O<sub>4</sub> 
where 0.0, 0.2, 0.4, 0.6, 0.8, 1.0. The optical 
properties were studied and from them it is 
obtained that the band gap decreases by addition of Cu(II). PL 
curves show that Cu<sub>x</sub>Zn<sub>1-x</sub>Al<sub>2</sub>O<sub>4</sub> 
where 0.0, 0.2, 0.4, 0.6, 0.8, 1.0 can be used in violet, blue 
and yellow applications. It is found also, Cu<sub>x</sub>Zn<sub>1-x</sub>Al<sub>2</sub>O<sub>4</sub> 
where 0.0, 0.2, 0.4, 0.6, 0.8, 1.0 nanoparticles are used as adsorbent to Cr(VI) 
from an aqueous solution to reach the maximum 
removal 86.75%. The second part is loading with CSs which 
prepared by one simple step method and verified by 
using FESEM. Here the effect of loading with CSs on 
Cu<sub>x</sub>Zn<sub>1-x</sub>Al<sub>2</sub>O<sub>4</sub> 
where 0.0, 0.2, 0.4, 0.6, 0.8, 1.0 was studied. The cubic structure does not change by 
loading of CSs. The crystal size becomes very small. 
According to morphology, there is a good 
good combination between Cu<sub>x</sub>Zn<sub>1-x</sub>Al<sub>2</sub>O<sub>4</sub> 
where 0.0, 0.2, 0.4, 0.6, 0.8, 1.0 nanoparticles and CSs which 
cause the decreasing in crystal size and band gap. 
However, there is no change in PL curves. CSs 
enhance the effect of Cu<sub>x</sub>Zn<sub>1-x</sub>Al<sub>2</sub>O<sub>4</sub> 
where 0.0, 0.2, 0.4, 0.6, 0.8, 1.0 nanoparticles on the removal of 
Cr(VI) from aqueous solution to reach the maximum 
removal 95.23%.

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Institute of Petroleum Nanotechnology Department.

Conflict of Interest: Authors clarify no conflict of 
interest.

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عناوين البحث
تحضير وفحص زنك الومينات مركبات نانو مستحدثة مخصصة بالحالة التحتية ومطعمة بأجزاء من الكربون باستخدام الترسيب المتضامن وتطبيقاتها في التحالب البنائية

المؤلفون: محمد عبد الجواد زايد, محمد محمد رشاد, ضياء ريان, شيماء محمود أبو عيطه

ملخص البحث
لقد تم في هذا البحث تحضير وفحص مركبات زنك الومينات النانوية في صورة نانو مستحدثة مخصصة بالحالة التحتية ومطعمة مايكونه من الكربون باستخدام الترسيب المتضامن والمعاملة الحرارية عند 1000 درجة مئوية لمدة ساعتين ثم دراسة تركيبها واستخدام عدد من أجهزة التحليك XRF ووضع الضيغة التركيبية لها Cu_{x}Zn_{1-x}Al_{2}O_{4} من حيث التركيب الجزيئي وتحليل العناصر المكونة بها باستخدام جهاز FT-IR الصيغة البنائية وطبيعة ترابط ذراتها بواسطة جهاز TEM ودراسة شكلها البلوري بواسطة جهاز XRD وكذلك تم دراسة الكوبوزات ونشاطها الضوئي بواسطة كل من الضوء العادي والأشعة فوق البنفسجية وكذلك أدائها مع الأنبثات الصناعي من ثم معرفة صيغتها وتنبيذها عنصرية وتنبيذها عنصرية من ثم معرفة التحليخ وتنبيذها عنصرية وتنبيذها عنصرية من.

وقال أن استخدامهم في تطبيقات عديدة وفعلاً تم تطبيقها في مجال ابحاث البيئة باستخدامها في زائدة الكربون المشمولي في بعض عيئات المياة المحتوية على هذا العنصر، ويتبعها نسبة الأزالة المتوقعة بغير صفات المركب المحضر تغير نسب مكاليماته وذلك باستخدام جهاز بلازما الحث ICP-AES وثبت النتائج نجاح التطبيق.

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