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Synthesis and Characterization of (Zn-Cr)and (Ni-Al) Nanoparticles for Water Sanitary Treatment Applications

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Abstract

Zn-Cr and Ni-Al layered double hydroxides (LDHs) with ratio 4:1and pH = 8 and pH = 9 respectively were prepared via co-precipitation technique**.** Thermal treatment at different temperature 100, 200, 300, 400, 500, and 600 °C created mixed metal oxide (MMO). The synthesized samples were examined using various approaches to determined its structural, morphological, and optical properties, as well as its toxicity.

X-ray diffraction (XRD) analysis exhibited that after Zn-Cr-LDH thermal treatment clearly formation the $ZnCr_2O_4$ spinal and hexagonal structure of metal oxide ZnO phases, while the $NiAl_2O_4$ spinal and cubic structure of metal oxide NiO phases evinced after Ni-Al-LDH thermal treatment.

The results of fourier transformation infrared spectroscopy (FT-IR) tests showed the lower frequency bands of the metal–oxygen and metal–oxygen–metal lattice vibrations bond confirming the LDHs transformed into mixed metal oxide structure upon calcination process for both compounds.

The field emission scanning electron microscopy (FE-SEM) examination revealed very wide size distribution and an irregular spherical shape particles within the nanoscale. With increase of annealing temperature promotes higher nanoparticle distribution density, growth, well-defined and fused of nanoparticles prepared, **,**moreover clear aggregation that caused nanograins with (a cauliflower-like) shape that could possibly lead to porous nature for both compounds. The average particles size of Zn-Cr LDH was 37.55 nm, where were 41.16 ,42 , 43.49,46.11 ,48.11 and 51.53 nm average particles size values at 100, 200, 300, 400, 500 and 600°C thermal treatment temperature respectively. The Ni-Al LDH average particles size was 31.52 nm, while were 35.64, 36.14, 41.84, 45.74 ,49.19

and 51.17 nm average particles size values at 100, 200, 300, 400, 500 and 600°C thermal treatment temperature respectively.

The atomic force microscopy (AFM) images confirmed a good distribution for nanoparticles on the surface and upon thermal treatment both values of particle size and surface roughness increase for both Zn-Cr-LDH and Ni-Al-LDH.

UV-Vis spectroscopy demonstrated a clear optical behavior for Zn-Cr-MMO-T in range 400-800 nm of the scanned wavelength in the visible region with pronounced blue-shift phenomenon which was attained along with increase of temperature from 100 °C up to 600 °C. Zn-Cr-LDH showed dual band gaps indirect 1.98 eV and direct 2.59 eV. The value of optical band gap for Zn-Cr-MMO-T exhibited clear reduction with increased thermal treatment temperature up to 500 °C. 2.11, 2.05, 2.08, 2, 1.97 eV were optical band gap values at thermal treatment temperature 100, 200, 300 ,400, 500 respectively. In 600 °C presented similar value that obtained at 500 °C. The Ni-Al-MMO-T revealed a clear optical behavior in the UV region 300 - 400 nm followed by a gradual decline in the range 400–800 nm with pronounced blue-shift phenomenon which was attained along with increase of temperature from 100 °C up to 600 °C for thermal treatment. The value of optical band gap for Ni-Al LDH was 3.2 eV. It is evident that the values of optical band gap for Ni-Al-MMO-T decreased with increased thermal treatment temperature up to 600 °C. 3.25, 3.10, 2.95, 2.85, 2.75, 2.65 eV represent band gap values at 100, 200, 300 ,400, 500, 600 for thermal treatment respectively.

Synthesized samples toxicity tested MTT assay with Lymphocytes and using exact half-dilution method. Six half-dose concentrations 2, 1, 0.5, 0.25, 0.125, 0.0625 µg/ml were used specifically for four samples Zn-Cr-LDH, Zn-Cr-MMO-600 Ni-Al-HDH and Ni-Al-MMO-600.At concentration0.0625 µg/ml cell viability were 93 % and 120 % for Zn-Cr-LDH and Zn-Cr-MMO-600, while were 88 % and 92 % for Ni-Al-HDH and Ni-Al-MMO-600. Based on MTT test results the half-maximal inhibitory concentration (IC_{50}) determined. The value of IC_{50} for Zn-Cr-LDH and Zn-Cr-MMO-600 were 98.53 µg/ml and 38.30 µg/ml, while were 17.06 µg/ml and 8.89 µg/ml for Ni-Al-LDH and Ni-Al-MMO-600 this means that toxicity decreases after thermal treatment.

This thesis investigated the efficient use of synthesized samples in water treatment operation by two main sections: First section photo degradation performance. Thermal transformation of LDHs into MMOs significantly improves effective photocatalyst for the degradation of organic pollutant (MO). Percentage degradation were 75% and 81% for treated with 400°C and 500 °C and demonstrated slight reduction 78% at 600 °C for Zn-Cr-LDH, where percentage degradation were 78 % , 77% and 80 % for treated with 400 °C , 500 °C and 600 °C for Ni-Al-LDH.

Second section antimicrobial potential of the LDH synthesized and their thermal treatment products were evaluated against a group of microorganisms included *Staphylococcus aureus* (Gram-positive), *Escherichia coli* (Gram-negative), *Candida albicans* (unicellular yeast), and *Penicillium digitatum* (filamentous fungus). The LDHs synthesized and their mixed metal oxides are effective in inhibition for the four cases and the diameter inhibition zone increases with the increasing of thermal treatment temperature and over time (at 48 hours). *Staphylococcus aureus* is more sensitive to Zn-Cr-LDH and Zn-Cr-MMO-T than *Escherichia coli*. Zn-Cr-MMO-600 demonstrating the highest inhibition diameter against *Staphylococcus aureus* was 40.21 mm, while against *Escherichia coli* was 29.28 mm at 48 hours. Zn-Cr-LDH and Zn-Cr-MMO-T proved to be more performance against *Candida albicans* than *Penicillium digitatum*. Zn-Cr-MMO-600 showed a high inhibition zone diameter against *Candida albicans* 35.22 mm and the Zn-Cr-MMO-500 sample also showed similar results 35.12 mm, while against *Penicillium digitatum* was 26.07 mm at 48 hours. Ni-Al-MMO-600 demonstrating the highest inhibition diameter against *Staphylococcus aureus* was 34.41 mm, while against *Escherichia coli* was 25.14 mm at 48 hours. Ni-Al-LDH and Ni-Al-MMO-T proved to be more effectiveness against Candida *albicans* than *Penicillium digitatum*. Ni-Al-MMO-600 showed a high diameter inhibition zone against *Candida albicans* 27.69 mm, while against *Penicillium digitatum* was 24.78 mm at 48 hours. The techniques and treatment methods characterized in this study are simple to use, potent and environmental friendly.

Chapter One

Introduction and Earlier Research

1.1 Introduction

The term nano used as a prefix for any unit for example a second or a meter, and its equal a billionth of that unit. The origin of the word (nano) is Greek which means an abnormally short person or dwarf. In a broad term, the materials with the individual particle or grain sizes bellow (100) nanometers know nanomaterials. Nanomaterials have unique properties such as low weight, high strength and high surface area, thus obtaining distinctive and important chemical and physical properties that are strikingly different from bulk materials. The science that studies, synthesizes and characterizes materials on the nanoscale is called nanotechnology [1]. Nanotechnology has a significant impact on the economy and society, as it has addressed many problems in a wide range of environmental, medical and industrial sectors such as biotechnology, drug delivery, electronic, smart materials, nano-manufacturing, electronics, energy and water [2].

In the 21st century, diminishing freshwater proportion stock and providing clean water remains a global challenge on account of declining water quality, increased population, and climate change especially in developing regions. Nanotechnology offers help build a sustainable future and water treatment landscape change through materials and devices with nanoscale with less energy, economically, and more effectively. Distinct techniques of nanomaterial-based developed for water treatment including nanomembrane filtration with nanopores that manifestation high selectivity and permeability for effective contaminants removal, adsorption that allows selectively adsorb contaminants, disinfection by targeting and inactivating microorganisms and catalysis through advanced oxidation operation for organic pollutants degradation [3-5].

1.2 Earlier Research

Ekta Tiwari et al. in (2020), studied remove plastic debris nanoparticles in (DI)water, synthetic hard water (SH) and synthetic freshwater (SF) by the Zn-Al- LDH that synthesized via coprecipitation technique at pH 8.The (TEM) and (FE-SEM) images showed the size of particles Zn-Al-LDH was less than 100 nm and while the size of NPDs 50 nm. X-ray diffraction results showed regular hexagonal structure. sorption capacity studied showed fast removal 164.49 mg/g and 162.62mg/g was observed in(SF)and (DI)water Whereas, it was least in(SH) 53 mg/g of Zn-Al- LDH for removal Nano-scale plastic debris (NPDs) in water system [6].

Tannaz Sadeghi Rad et al., (2020), prepared Zn-Cr-LDH, Zn-Cr-LDH/BC, and Zn-Cr-LDH/CNT by co-precipitation method at pH=9 as sonophotocatalytic decomposing refractory pollutants. XRD analysis confirmed high crystallinity of the samples, EDX consented successful preparation of nanocomposites homogeneous distribution of elements Zn, Cr, and C, SEM and TEM images showed porous prepared nanocomposites. In Zn-Cr-LDH/BC sonophotocatalytic process, the degradation efficiency of rifampicin (RF) was (100%) within 40 min, (150 W) ultrasound and visible light irradiation [7].

Tarmizi Taher et al, (2020), prepared Zn-Cr-LDH and Zn-Al-LDH using coprecipitation at pH=10 and with ratio (3:1) of each LDHs. XRD analysis confirmed the synthesized layered double hydroxides have good crystallinity. The FT-IR spectrum results showed Zn-Cr- LDH and Zn-Al-LDH interlayer space were dominated by (CO_3) as the interlayer anion species. Experimental data fit well with the Freundlich isotherm. Highly influenced of adsorption operation toward the ion exchange caused less activity adsorption capacity of Zn-Cr-LDHs against Congo red dye although a higher surface area of Zn-Cr- LDH [8].

C. Gomez-Polo et al., (2020), examined influence Cr, N and Cr/N doping TiO_2 nanoparticles on antibacterial action, photocatalytic and the adsorption capacity.N-TiO_2, Cr-TiO_2 and N/Cr-TiO_2 NPs were prepared via sol gel technique Then thermally treated for two hours at 632 K. X-ray diffraction results disclosed the crystallite sizes range were (6, 6and 9) nm for Cr and N/Cr and N doping specimens. TEM images showed a nearly spherical shape of prepared nanoparticles. The BET test confirmed adding chromium caused lucid rise of surface area which were (80, 125 and 137) m^2/g of N-TiO_2, Cr-TiO_2 and Cr/N-TiO_2 respectively. UV–Vis Analysis results showed that the band gap of N-TiO_2, Cr-TiO_2 and N/Cr-TiO_2 were1.6, 1.1, 1.5 respectively. Doping specimens showed highest adsorption capacity and photocatalytic activity to methyl orange dye. The antibacterial activity was studied against Escherichia coli, result confirmed bacteriostatic and bactericidal activity of Cr-TiO_2 samples [9].

Lekbira EL Mersly et al., (2021), studied water treatment by adsorption photocatalysis process against organic pollutants .Zn-Cr-X LDHs where (X ¼ Cl, SO_4 and CO_3) prepared via a co-precipitation chemical method at pH=5.5 XRD analysis showed that all prepared phases Zn-Cr-Cl, Zn-Cr-CO_3 and Zn-Cr-SO_4 LDHs were with hexagonal lattice. The band gap of Zn-Cr-Cl, Zn-Cr-CO_3 and Zn-Cr-SO_4 LDHs were 2.13eV, 1.97eV and1.90eV respectively which calculated from the diffuse-reflectance spectra of UV results. TEM images indicated the particle size changes (13, 62 and 70) nm According to nature of the intercalated anion Cl, SO_4 and CO_3 respectively. The adsorption percentage of acid orange 7 (AO7) was 25% for Zn-Cr-SO_4, 32% for Zn-Cr-CO_3 and 49.5% for the most effective photocatalyst Zn-Cr-Cl [10].

Angela Spoială et al., (2021), prepared ZnO nanoparticles by co-precipitation approach. X-ray diffraction results confirmed the wurtzite hexagonal of ZnO nanoparticles structure with average crystallite size about 19 nm. The TEM images exhibited a particle size were in ranging (20-30) nm, while The SEM images obtained micrometric agglomerations for preparing nanoparticles with a polyhedral-shaped manner. Fourier transform infrared spectroscopy exhibited the wave number (462–419 cm^{-1}) was for Zn-O stretching vibration bond. ZnO nanoparticles showed good degradation capability 91% as photocatalysts against methyl orange dye (MO). Antibacterial activity of ZnO NPs was tested against yeast *Candida* and two different types of bacteria *Escherichia coli* (Gram-negative) and *staphylococcus aureus* (Gram-positive). The strongest activity for preparing nanoparticles was found against *S. aureus* with inhibition zone diameter 19mm [11].

Somia Djelloul Bencherif et al., (2021), synthesized (Zn-Cr) layered double hydroxide by co-precipitation technique and calcined at 500 ^{0}C From XRD patterns, Zn-Cr- LDH presented a hexagonal structure. The layered morphology of Zn-Cr-LDH was observed in TEM images and small nanoparticles was obtained after the thermal treatment. Moreover SEM revealed a strong agglomeration in the layered sample. In addition, the homogeneous distribution of Zn and Cr in the samples was confirmed by EDX coupled to electron microscopy techniques. The FTIR spectra of samples confirmed deformation and translation modes of (M-OH) and (M-O-M) bonds forming below (1000) cm^{-1}. The UV–Vis DRS Analysis results showed that the band gap of Zn-Cr-LDH 2.53 eV and Zn-Cr-500 1.83 eV. In photodegradation tests Zn-Cr-500 showed high photocatalytic activity to crystal violet dye (87.7%) [12].

Yulizah Hanifah et al., (2022), synthesized NiAl-[$SiW_{12}O_{40}$] and NiAl-[$PW_{12}O_{40}$]layered double hydroxide polyoxometalate by co precipitation approach at pH=10. DR-UV analysis showed the band gap decreased from 4.76 eV for NiAl pristine than to 3.22 eV for NiAl-[$SiW_{12}O_{40}$] and 3.78 eV for NiAl-[$PW_{12}O_{40}$]. The FTIR spectra confirmed the absorption band in 500 to 800 cm^{-1} represented the stretching vibration (M−O), (M−O−M) and (O−M−O). SEM images validated microsphere to the layered structure of all LDH samples. NiAl-[$SiW_{12}O_{40}$] and NiAl-[$PW_{12}O_{40}$] layered double hydroxide showed improving degradation photocatalytic performance compared to layered double hydroxide pristine. The percentage degradation of Malachite Green (MG) were 68.94% for Ni-Al LDH pristine, 84.51% for Ni-Al-[$PW_{12}O_{40}$]and 88.91% for NiAl-[$SiW_{12}O_{40}$][13].

Sujeong Kim et al., (2022), studied removing methyl blue daye (MB) from polluted water and antibacterial activity for ZnO nanoparticles. ZnO NPs prepared with different presence (1–4) M of NaOH by sol-gel technique. XRD analysis confirmed hexagonal wurtzite-structured for ZnO nanoparticles and crystal sizes of ZnO–1M, ZnO–2M, ZnO–3M, and ZnO–4M were (22, 18, 19, and 19) nm respectively. TEM images showed nearly circular particle shape of (ZnO–1M) with presence of 1.0 M NaOH, while the needle shaped ZnO when NaOH concentration increases. The UV–Vis DRS Analysis results showed that the band gap value was 3.18, 3.24, 3.24and 3.23 of ZnO–1M, ZnO–2M, ZnO–3M, and ZnO–4M. Methyl blue daye (MB) was degraded by ZnO–1M with a greater percentage degradation 95%. 96.43% was ZnO–4M sterilization performance against S. aureus, where 95.72% was ZnO–4M sterilization performance against E. coli [14].

Khaled et al., (2022), synthesized Zn-doped TiO_2 nanoparticles by the Sol-gel calcined at 450 ^{0}C for 4 h. The FTIR analysis showed appearance of bending vibration (Ti-O-Ti) at 495 cm^{-1} and stretching band (Zn-O) at 470 cm^{-1}. XRD analysis exhibited an average particle size range (22-30) nm of TiO_2 nanoparticles and that decreased to an average particle size range (16-27.5) nm after doping. BET technique results showed a high surface area for zinc-doped TiO_2 (~26.76) m^2. g^{-1} compared to TiO_2 surface area (15.51) m^2. g^{-1}. In wastewater treatment application 68.2%, 71.1% and 75.1% were adsorption activity removal results of SLS, ofloxacin and methylene blue respectively [15].

Sura Sabri Hasson et al., (2022), synthesized Nickel oxide NPs by sol-gel method at 75 °C and pH 12. Both SEM and AFM images showed that nanoparticles size in the range (26.80-37.96) nm. X-ray diffraction results disclosed the cubic structure of NiO. 3.45 eV was the value of optical band gap as UV-VIS spectra results confirmed.Fourier transform infrared spectroscopy exhibited NiO band at 627 cm^{-1} [16].

Richa Kothari et al., (2022), synthesized green Cr_2O_3 nanoparticles by used the aqueous environment of cinnamon and chromium (III). X-ray diffraction showed a hexagonal structure of prepared green Cr_2O_3 nanoparticles average particle size 48 nm. TEM images exhibited an average particle size 48 nm of Cr_2O_3 nanoparticles and oval-shaped structure. The FTIR spectra confirmed the presence of C=O stretching and Cr-O stretching vibrations. Antibacterial activity studied against Escherichia coli, Bacillus subtilis and Pseudomonas aerugenosa. A better Zone inhibition (27mm) was against Pseudomonas aerugenosa [17].

Stanslaus G. Mtavangu et al., (2022), prepared Ag-ZnO nanocomposites by aqueous extract of (Tetradenia riperia) leaf using aqueous extract of leaf in addition their antimicrobial potential tested toward *Staphylococcus aureus* and *Escherichia coli*. This work showed influence pH, concentration and temperature. Ag-ZnO nanocomposites was examined via FTIR, FE-SEM, TEM and XRD. The results revealed 80 ^{0}C, pH(7-8) and Ag concentration 8% were optimal for synthesized Ag-ZnO nanocomposites. X-ray diffraction results showed particle size reduction (23.6 to 14.8) nm by Ag-ZnO nanocomposites increasing and FESEM analysis agreed that. TEM images determined average of particles size was 14.8 nm. Antimicrobial activity of AgZnO nanoparticles revealed a strong antimicrobial capability against *coli Escherichia* comparing *Staphylococcus aureus*. Tetradenia riperia is suitable for Ag-ZnO nanocomposites fabrication that is employed for diverse using like purification of water[18].

Anna Maria Cardinale et al., (2023), prepared Zn-Al-SO_4-LDH, Zn-Al-CrO_4 -LDH, Zn-Al-MMO and Zn-Al-MMO-CrO_4 by co-precipitation method at pH 8±0.5 and thermal annealing at 450 ^{0}C. The FE-SEM exhibited Morphology of the annealed LDHs. The EDXS analysis confirmed formed mixed oxide. The antibacterial activity was studied for Zn-Al-SO_4 LDH and Zn-Al-MMO against Gram-negative Escherichia coli and Gram-positive Staphylococcus aureus. Zn-Al-SO_4-LDH inhibition diameter was 1.79 cm, while for ZnAl-MMO was 3.1 cm against Escherichia coli which showed a greater effect than Staphylococcus aureus 2.3 cm for Zn-Al-MMO. Percentage degradation the adsorption percentage of MO dye was 84 % for Zn-Al-SO_4-LDH, 88 % for Zn-Al-MMO, 76 % for Zn-Al-CrO_4-LDH, and 92 % for Zn-Al-MMO-CrO_4 [19].

Yuquan Wang et al., (2023), prepared a highly adsorbent photocatalytic $BiVO_4$/Mg-Al-LDHs by co-precipitation approach with 2:8, 3:7, and 5:5 ratios and temperature calcination 300, 400, 500, and 600 ^{0}C. XRD analysis confirmed high crystallinity of the samples, TEM images showed Mg-Al-LDHs were hexagonal plates with surface sizes 2 μm and an irregular block structure of $BiVO_4$ has formed by the particles aggregation. The UV–Vis DRS Analysis results showed that the band gap of BiVO4/Mg-Al-LDHs 2.09 eV and$BiVO_4$ 2.05 eV. $BiVO_4$/Mg-Al-LDHs showed excellent photocatalytic performance than the pristine $BiVO_4$ and Mg-Al-LDHs. Different MB initial concentrations (5, 10, 15, and 20) mg/L were used to study the adsorption capacity and photocatalytic activity, In 10 mg/L, the percentage of methylene blue dye (MB) adsorbed in 20 min was 66.1% and 92.4% during 100 min of photolysis and the ratio of adsorption-degradation was 86% [20].

Iqra Batool et al., (2024), studied removing methyl orange dye (MO) from polluted water and antibacterial activity for prepared materials. The NiAl-LDH prepared by co-precipitation method, while NiAl-LDH/Cu-MOF by a simple thermal impregnation strategy. The UV–Vis DRS Analysis results showed that the NiAl-LDH band gap (1.91 eV), Cu-MOF (2.54 eV), and 1.38 eV for NiAl-LDH/Cu-MOF catalyst. (MO) was degraded by NiAl-LDH alone with percentage degradation 94%, Cu-MOF 82% and NiAl-LDH/Cu-MOF showed excellent degradation capability 99%. By disk diffusion method, antibacterial activity were studied against Staphylococcus aureus, Enterococcus faecalis (Gram positive) and Escherichia coli, Pseudomonas fluorescens (Gram negative). The results signalized that Gram-negative bacteria was more vulnerable to the Ni-Al-LDH/Cu-MOF due to positive charge of this bacteria [21].

Sonya Dadakhani et al., (2024), synthesized histidine His/Zn-Cr-LDH by coprecipitation process. The FE-SEM exhibited displays accumulated disk-like shape with submicron size for Zn-Cr-LDH and His/Zn-Cr-LDH. The antibacterial activity was studied in rat injury experiments depending on disk diffusion method for 12 h with various groups (GU, Glu + GOx, GOx, His/ Zn-Cr-LDH, His/Zn-Cr-LDH + Glu, His/Zn-Cr-LDH + GOx, Zn-CrLDH + Glu + GOx, and His/ZnCr-LDH + Glu + GOx). Inhibition rates of Glu and GOx were 90.62% in the presence of for S. aureus and 84.61% for E. coli. Results showed that His/Zn-Cr-LDH possibility expedite the disinfection and curing of spoiled wounds and could an appropriate for treating diabetic ulcer wounds [22].

Wakeel Ahmad et al., (2024), prepared Zn-Fe-LDHs by coprecipitation technique with a ratio1:1at pH∼12. X-ray diffraction results disclosed the successful Zn-Fe-LDHs formation with highly crystalline structure. The FTIR spectra confirmed appeared the vibrations band of (M−OH), (M−O) and (M−O−M) in 703 cm^{-1} and 472 cm^{-1} which associated with the brucite-likes structure of LDH. The UV–Vis Analysis results showed that the band gap of Zn-Fe-LDHs, PVP/LDH and Ag-doped (1, 3, and 5wt %) samples were 2.81, 2.70, 2.57, 2.47, and 2.38 eV respectively. The TEM images provided the hexagonal plate-like structure of Zn-Fe-LDHs, adding PVP to Zn-Fe-LDHs looks like a lamellar structure and a gradual increase in an agglomeration with incorporating Ag into PVP/LDH. Percentage degradation of Rhodamine B (RhB) dye were in (neutral media and pH = 7) 69.7, 76.8, 89.3, 91.5, and 92.6%, in (acidic media and pH = 3) 60.3, 69.6, 85.9, 88.9, and 90.3% and in (basic media and pH = 12) 60.8, 70.8, 85.6, 86.9, and 94.8% for Zn-Fe-LDHs, PVP/LDH and Ag-doped (1, 3, and 5wt %) respectively. The antibacterial activity was studied against Gram-negative Escherichia and a greater inhibition diameter was 3.65 mm for Ag-doped (5wt %) sample [23].

Xinmiao Yu et al., (2024), synthesized spinel $NiAl_2O_4$ via the polyacrylamide gel approach and studied the effects of different salts ($NiSO_4 \cdot 6H_2O$), $NiSO_4$, ($Al_2(SO_4)_3 \cdot 18H_2O$) and ($Al(NO_3)_3 \cdot 9H_2O$) on characteristics and photocatalytic activity of preparing material. SEM and TEM images showed particles size of spinel $NiAl_2O_4$ were with an average about 10 nm and approximately spherical. A greater degradation percentage of tetracycline hydrochloride (TC) was 86.3% of spinel $NiAl_2O_4$ with $Al_2(SO_4)_3 \cdot 18H_2O$ and $NiSO_4 \cdot 6H_2O$ salts. Toxicity test (T.E.S.T.) showed that the (TC) photocatalytic degradation in wastewater by prepared spinel could using for water purification [24].

Raman Duddi et al., (2025), studied using of porous Ni-Al layered double hydroxide as an efficient pseudo capacitive material. Ni-Al-LDH prepared by a single-step hydrothermal technique with ratio of 3:1. X-ray diffraction results revealed hydrotalcite-like structure in two-dimensional (2D). The SEM images demonstrated a high nano-crystallized of Ni-Al-LDH and possess a distinctly porous structure. BET technique exhibited a high surface area (~117.4) $m^2. g^{-1}$. TEM images exhibited nano-structure of Ni-Al-LDH and a porous and well-organized arrangement. At low current densities, after 10,000 (charge/discharge cycles) Ni-Al-LDH electrode retains (91 %) of its initial capacitance [25].

1.3 Aim of the study

The aim of this study is to each of Zn-Cr and Ni-Al nano biomaterials synthesized by co-precipitation chemical method in water treatment. Nano biomaterials are synthesized and characterized by the proper techniques for studying structural, morphological, optical properties in addition to evaluating its performance as photodegradative and their antimicrobial potential. Implement a photodegradation test on a pollutant model (organic dye) and detect antimicrobial activity and that prepared nanoparticles are suitable for the required applications.

الخلاصة

تم تحضير هيدروكسيدات مزدوجة الطبقات من الزنك-الكروم والنيكل-الألمنيوم بنسبة 4:1 ودرجة حموضة تساوي 8 و9 على التوالي، باستخدام تقنية الترسيب المشترك، نتج عن المعالجة الحرارية عند درجات حرارة مختلفة (100، 200، 300، 400، 500،600) درجة مئوية اكسيد معدني مختلط. فُحصت العينات المُحضرة باستخدام طرائق مختلفة لتحديد خصائصها البنيوية والمورفولوجية والبصرية، بالإضافة إلى سُميتها.

أظهر تحليل حيود الأشعة السينية (XRD) **أن** بعد المعالجة الحرارية ل Zn-Cr-LDH تشكلت بوضوح أطوار التركيب السداسي لأكسيد المعدن ZnO و التركيب السبينيل$ZnCr_2O_4$ ، بينما ظهرت أطوار التركيب المكعب لNiO و التركيب السبينيل لـNiAl2O4 بعد المعالجة الحرارية لNi-Al-LDH.

أظهرت نتائج اختبارات مطيافية الأشعة تحت الحمراء لتحويل فورييه (FT-IR) أن النطاقات الترددية المنخفضة لاهتزازات الشبكة المعدن - أكسجين والمعدن - الأكسجين - معدن تؤكد تحول LDHs إلى بنية أكسيد معدني مختلط عند عملية التكليس لكلا المركبين.

كشف فحص المجهر الإلكتروني الماسح الباعث للمجال (FE-SEM) عن توزيع واسع جدًا للحجم و شكل كروي غير منتظم للجسيمات ضمن المقياس النانوي. مع زيادة درجة حرارة التلدين، تتعزز كثافة توزيع الجسيمات النانوية ونموها، بالإضافة إلى تحديدها جيدًا واندماجها، بالإضافة إلى تجمع واضح تسبب في حبيبات نانوية ذات شكل (يشبه زهرة القرنبيط) مما قد يؤدي إلى طبيعة مسامية لكلا المركبين. كان متوسط حجم جسيمات Zn-Cr LDH 37.55 نانومتر، في حين كانت قيم متوسط حجم الجسيمات 41.16 و42 و43.49 و46.11 و48.11 و51.53 نانومتر عند درجة حرارة المعالجة الحرارية 100 و200 و300 و400 و500 و600 درجة مئوية على التوالي. كان متوسط حجم جسيمات Ni-Al LDH 31.52 نانومتر، بينما كانت 35.64، 36.14، 41.84، 45.74، 49.19 و51.17 نانومتر متوسط قيم حجم الجسيمات عند درجات حرارة المعالجة الحرارية 100، 200، 300، 400، 500 و600 درجة مئوية على التوالي.

أكدت صور مجهر القوة الذرية (AFM) توزيعًا جيدًا للجسيمات النانوية على السطح، وعند المعالجة الحرارية، ازدادت قيم حجم الجسيمات وخشونة السطح للكل من Zn-Cr-LDH وNi-Al-LDH.

أظهر التحليل الطيفي للأشعة فوق البنفسجية والمرئية (UV-Vis) سلوكًا بصريًا واضحًا لـ Zn-Cr-MMO-Tفي نطاق 400-800 نانومتر من الطول الموجي الممسوح ضوئيًا في المنطقة المرئية مع ظاهرة انزياح أزرق واضحة والتي تم تحقيقها مع زيادة درجة الحرارة من 100 درجة مئوية إلى 600 درجة مئوية. أظهر Zn-Cr-LDH فجوة طاقة مزدوجة غير مباشرة 1.98 إلكترون فولت ومباشرة 2.59 إلكترون فولت. أظهرت قيمة فجوة الطاقة البصرية لـ Zn-Cr-MMO-T انخفاضًا واضحًا مع زيادة درجة حرارة المعالجة الحرارية حتى 500 درجة مئوية. كانت قيم فجوة الطاقة البصري 2.11 و 2.05 و 2.08 و 2 و 1.97 إلكترون فولت عند درجة حرارة المعالجة الحرارية 100 و 200 و 300 و 400 و 500 على التوالي. في 600 درجة مئوية ظهرت قيمة مماثلة لتلك التي تم الحصول عليها عند 500 درجة مئوية. أظهر Ni-Al-MMO-T سلوكًا بصريًا واضحًا في نطاق الأشعة فوق البنفسجية 300-400 نانومتر، تلاه انخفاض تدريجي في النطاق 400-800 نانومتر، مع ظاهرة انزياح أزرق واضحة، والتي تم تحقيقها مع زيادة درجة الحرارة من 100 درجة مئوية إلى 600 درجة مئوية للمعالجة الحرارية. بلغت قيمة فجوة الطاقة البصرية لـ Ni-Al LDH 2 .3 إلكترون فولت. ومن الواضح أن قيم فجوة الطاقة الضوئي لـ Ni-Al-MMO-T انخفضت مع زيادة درجة حرارة المعالجة الحرارية حتى 600 درجة مئوية. تمثل القيم 3.25، 3.10، 2.95، 2.85، 2.75، 2.65 إلكترون فولت قيم فجوة الطاقة عند 100، 200، 300، 400، 500، و600 للمعالجة الحرارية على التوالي.

تم اختبار سُمية العينات المُحضرة باستخدام اختبار MTT والخلايا الليمفاوية، وذلك باستخدام طريقة التخفيف النصفي الدقيق. استُخدمت ستة تراكيز نصفية (2، 1، 0.5، 0.25، 0.125، 0.0625) ميكروغرام/مل خصيصًا لأربع عينات Zn-Cr-LDH، وZn-Cr-MMO-600 وNi-Al-HDH و Ni-Al-MMO-600.عند التركيز 0.0625 ميكروغرام/مل ، بلغت الفعالية الحيوية للخلايا % 93 و%120 لكل من Zn-Cr-LDH وZn-Cr-MMO-600، بينما بلغت %88 و% 92 لكل من Ni-Al-HDH وNi-Al-MMO-600بناءً على نتائج اختبارMTT ، تم تحديد التركيز النصفي المثبط الأقصى (IC_{50}) .بلغت قيمة التركيز النصفي المثبط الاقصى لZn-Cr-LDH وZn-Cr-MMO-600 98.53 ميكروجرام/مل و 38.30 ميكروجرام/مل، بينما كانت 17.06 ميكروجرام/مل و 8.89 ميكروجرام/مل لـ Ni-Al-LDH و Ni-Al-MMO-600وهذا يعني أن السُمية تنخفض بعد المعالجة الحرارية.

تتناول هذه الاطروحة الاستخدام الفعال للعينات المُحضرة في معالجة المياه من خلال قسمين رئيسيين: القسم الاول فعالية أداء التحلل الضوئي. يُحسن التحول الحراري لLDHs إلى MMOs كفاءة التحفيز

الضوئي في تحلل الملوث العضوي (MO) بشكل ملحوظ. بلغت نسب التحلل 75 % و81% عند المعالجة بدرجات حرارة 400 و500 درجة مئوية، بينما أظهرت انخفاضًا طفيفًا بنسبة 78% عند 600 درجة مئوية لـZn-Cr-LDH ، بينما بلغت نسب التحلل 78% و77% و80% عند المعالجة بدرجات حرارة 400 و500 و600 درجة مئوية لـNi-Al-LDH.

في القسم الثاني، تم تقييم القدرة المضادة للميكروبات لـ LDH المُحضرة ومنتجات معالجتها الحرارية ضد مجموعة من الكائنات الحية الدقيقة تتضمن المكورات العنقودية الذهبية (موجبة الجرام)، والإشريكية القولونية (سالبة الجرام)، والمبيضة البيضاء (خميرة وحيدة الخلية)، والبنسليوم الإصبعي (فطر خيطي). كانت LDHs المُحضرة وأكاسيدها المعدنية المختلطة فعّالة في التثبيط في الحالات الأربع، ويزداد قطر منطقة التثبيط مع زيادة درجة حرارة المعالجة الحرارية ومع مرور الوقت (بعد 48 ساعة). تُعد المكورات العنقودية الذهبية أكثر حساسية لـ Zn-Cr-LDH و Zn-Cr-MMO-T من الإشريكية القولونية. أظهر Zn-Cr-MMO-600 أعلى قطر تثبيط ضد المكورات العنقودية الذهبية، حيث بلغ 40.21 مم، بينما بلغ ضد الإشريكية القولونية 29.28 مم بعد 48 ساعة. أثبت Zn-Cr-LDH و Zn-Cr-MMO-T فعاليةً أكبر ضد المبيضة البيضاء مقارنةً بـ .Penicillium digitatum أظهر Zn-Cr-MMO-600 قطر تثبيط عالٍ ضد المبيضة البيضاء بلغ 35.22 مم. وأظهرت عينة Zn-Cr-MMO-500 نتائج مماثلة، حيث بلغ قطر التثبيط 35.12 مم، بينما بلغ قطر التثبيط ضد فطر Penicillium digitatum 26.07 مم بعد 48 ساعة. وأظهر Ni-Al-MMO-600 أعلى قطر تثبيط ضد بكتيريا Staphylococcus aureus ، حيث بلغ 34.41 مم، بينما بلغ قطر التثبيط ضد بكتيريا Escherichia coli 25.14 مم بعد 48 ساعة. وأثبت كلٌ من Ni-Al-LDH وNi-Al-MMO-T فعالية أكبر ضد فطر Candida albicans مقارنةً بفطر Penicillium digitatum وأظهر Ni-Al-MMO-600 منطقة تثبيط عالية القطر ضد فطر Candida albicans ، حيث بلغ قطرها 27.69 مم، بينما بلغ قطرها ضد فطر Penicillium digitatum 24.78 مم بعد 48 ساعة . التقنيات وطرائق المعالجة الموصوفة في هذه الدراسة سهلة الاستخدام وفعالة وصديقة للبيئة.

جمهورية العراق
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قسم الفيزياء

تحضير وتوصيف جسيمات (Zn-Cr)و(Ni-Al)النانوية لتطبيقات معالجة المياه الصحية

أطروحة مقدمة الى

مجلس كلية العلوم–جامعة ديالى

وهي جزء من متطلبات نيل درجة الدكتوراه فلسفة في علوم الفيزياء

من قبل

أسرار جبار موات

بكالوريوس علوم فيزياء ٢٠٠٧ م
ماجستير علوم فيزياء ٢٠٢١ م

بإشراف

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