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Research Paper

Synthesis and Characterization of Ni/Al Layered Double Hydroxides Composite Based-Material with Chitosan, Cellulose, and Graphene Oxide

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Abstract
In this study, the synthesis of composite materials produced from Ni/Al with three types of carbon-based materials namely chitosan (Ch), cellulose (Ce), and graphene oxide (GO) was successfully carried out supported by X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR), and Brunauer-Emmett-Teller (BET) analysis. The combined characteristics of the two starting materials are present in the composite material based on XRD and FT-IR data. The surface area of Ni/Al-LDH increased after compositing with Ch, Ce, and GO, from 3.3 m^2/g to 9.5 m^2/g in Ni/Al-Ch, 5.1 m^2/g in Ni/Al-Ce, and 78.4 m^2/g in Ni/Al-GO. These findings indicate that the materials are suitable for various applications such as photocatalytic and adsorption as effective materials in further research.

Keywords
Layered Double Hydroxide, Characterization, Chitosan, Cellulose, Graphene Oxide

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1. INTRODUCTION

Layered double hydroxides (LDHs) are two-dimensional materials having a brucite-like structure, made up of uniformly distributed metal cations with interlayer gaps filled with anions and solvent molecules (Houssaini et al., 2024; Kameliya et al., 2023; Soulé et al., 2024). LDHs have remarkable features such as large surface area, changeable composition, and biocompatibility, making them useful in a variety of applications including catalysis, adsorption, and environmental remediation (Kim et al., 2024; Mishra et al., 2018; Xie et al., 2024). The typical formula for LDH is $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A^{n-})_{x/n}.mH_2O$, where M(II) and M(III) are divalent and trivalent metal cations, respectively, A^{n-} is the interlayer anion, and x is the molar ratio of M(III) to total metal ions (Bian et al., 2023; Cogal et al., 2024). Because of its adjustable features and high reactivity, LDH has found significant use in a variety of sectors.

The use of LDH applications in the application process is extremely limited due to the lack of functional groups and structural components in pure LDH, as well as the ease with which the coating can be peeled off, resulting in a less efficient process. To address these flaws, LDH is changed by adding functional groups or structural components. Various forms of carbon can be utilized to address these flaws (Karim et al., 2022; Siregar et al., 2022b; Tan et al., 2024).

Chitosan (Ch), also known as deacetylated chitin, is a naturally occurring biopolymer that is non-toxic, renewable, and biodegradable. Chitosan's numerous amino and hydroxyl groups allow for excellent complexation and coordination with heavy metals and composite materials. However, chitosan's usage is limited by its low mechanical resistance, instability, and material regeneration problems (Yu et al., 2024).

The most common biopolymer, cellulose (Ce), has been highlighted as a potential environmentally acceptable material for adsorption applications because of its many readily modifiable hydroxyl groups (Salama, 2023). Graphene oxide (GO) is a very fascinating carbon structure with oxygen groups connected to it (carboxyl, epoxy, hydroxyl, phenol), and sp^2 and sp^3 hybridized carbon atoms (Amri and Hanifah, 2023). According to Avornyo and Chrysikopoulos (2024), the efficacy of GO in the removal of contaminants from effluent can be enhanced through functionalization or modification.

This study aims to conduct the modification of layered double hydroxide (LDH), namely Ni/Al-LDH, using carbon-based materials such as chitosan, cellulose, and graphene oxide. This is done to demonstrate the efficacy of composite material preparation in enhancing performance in practical use. The investigation was undertaken by producing the materials and analyzing their characteristics using X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), and Brunauer-Emmett-Teller (BET)

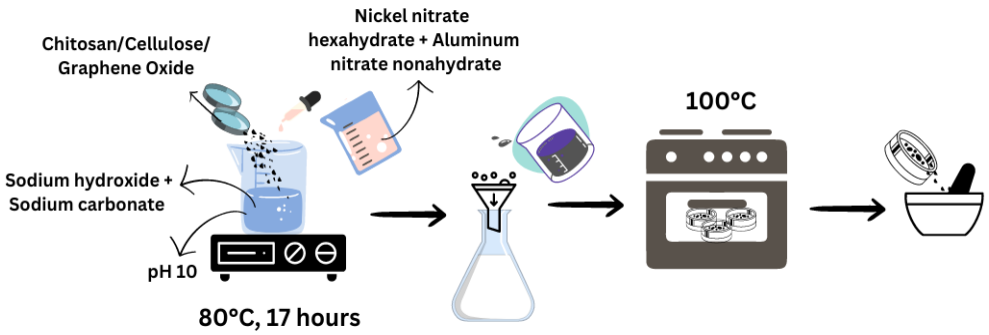

Figure 1. The Illustration of the Preparation of Ni/Al-(Chitosan/Cellulose/Graphene Oxide) Composite

analysis.

2. EXPERIMENTAL SECTION

2.1 Chemical and Instrumental

The chemicals utilized in this investigation included nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$), aluminum nitrate nonahydrate ($Al(NO_3)_3.9H_2O$), sodium hydroxide (NaOH), and sodium nitrate ($NaNO_3$) procured from Sigma Aldrich. Merck provided microcrystalline cellulose $(C_6H_{10}O_5)n$, sodium carbonate (Na_2CO_3), and potassium permanganate ($KMnO_4$). The graphite was acquired from Bukata Organic Indonesia. A 30% hydrogen peroxide solution was acquired from Smart-LAB. Mallinckrodt provided hydrochloric acid (HCl). Chitosan derived from the exoskeleton of shrimp. The distilled water (H_2O) was acquired from Brataco, an Indonesian source. The research utilizes Fourier Transform Infrared (FTIR) analysis using a Shimadzu Prestige-21 instrument, Surface Area and Pore Size analysis using a BET instrument of type NOVA 4200e, and X-Ray Diffraction (XRD) analysis with a Rigaku Miniflex-6000 instrument.

2.2 Synthesis of Ni/Al-LDH

The mixture consisted of 100 mL of a 0.3 M solution of $Ni(NO_3)_2.6H_2O$ and 100 mL of a 0.1 M solution of $Al(NO_3)_3.9H_2O$, which were added gradually to a mixture of 50 mL of a 2 M solution of NaOH and 100 mL of a 0.3 M solution of Na_2CO_3. Subsequently, the pH of the solution was modified by introducing a 2 M NaOH solution until it reached a pH of 10. The mixture was agitated for a duration of 17 hours and then maintained at a temperature of 80°C. Subsequently, the specimen underwent filtration and rinsing with distilled water before being subjected to heating in an oven at a temperature of 100°C.

2.3 Extraction of Chitosan (Siregar et al., 2022a)

The extraction of shrimp shells involved demineralization and deproteination procedures. The shrimp shells were pulverized and placed into a beaker, followed by the addition of 1 M HCl in a 1:10 (weight/volume) ratio. The solution was agitated at a temperature of 60°C for a duration of 3 hours. Once the stirring process is finished, the solid particles are separated from the liquid by filtration and then subjected to a drying process. Once the demineralization process has concluded, it is then succeeded by the deproteination process. The remaining substance obtained after the demineralization process was transferred into a container called a beaker. Then, a solution of sodium hydroxide (NaOH) with a concentration of 0.1 M was added to the beaker in a ratio of 1 part substance to 10 parts solution by weight/volume. The solution was agitated at a temperature of 60°C for a duration of 1 hour. After a duration of 1 hour, the solid particles were separated from the liquid by passing it through a filter and subsequently subjected to the process of drying in a heated oven. The chitosan extracted from shrimp shells was analyzed using XRD, FTIR, and BET techniques to confirm its successful extraction.

2.4 Synthesis of Graphene Oxide

The Hummers method, as modified by Yang and Cao (2022), was employed to synthesize graphene oxide. 3 grams of graphite and 1.5 grams of $NaNO_3$ were combined in a glass beaker. Then, 69 mL of H_2SO_4 was added and mixed until the mixture was uniform. A total of 9 grams of $KMnO_4$ was gradually introduced at a temperature lower than 20°C. The mixture was agitated for a duration of 7 hours at a temperature of 35°C. An additional 9 grams of $KMnO_4$ was introduced into the mixture and agitated for a duration of 14 hours. The resulting mixture was let to stand at ambient temperature and gradually supplemented with 400 mL of distilled water and 3 mL of H_2O_2. During the subsequent step, the mixture underwent filtration and was rinsed with distilled water. It was then subjected to drying in an oven at a temperature of 65°C for a duration of 72 hours.

2.5 Preparation Ni/Al-(Chitosan/Cellulose/Graphene Oxide)

30 mL of a 0.75 M solution of $Ni(NO_3)_2.6H_2O$ and 30 mL of a 0.25 M solution of $Al(NO_3)_3.9H_2O$ were combined in a beaker. Then, 2 M NaOH was gradually introduced to the mixture until the pH reached 10. The mixture was agitated for 1 hour. Subsequently, a total of 3 grams of carbon-based materials, namely chitosan, cellulose, and graphene oxide, were introduced into the mixture and agitated for a duration of 3 days at a temperature of 80°C. The resultant precipitate was subjected to filtration and rinsed with distilled water, followed by heating in an oven at a temperature of 100°C. The illustration of the preparation of

Ni/Al-(Chitosan/Cellulose/Graphene Oxide) composite is shown in Figure 1.

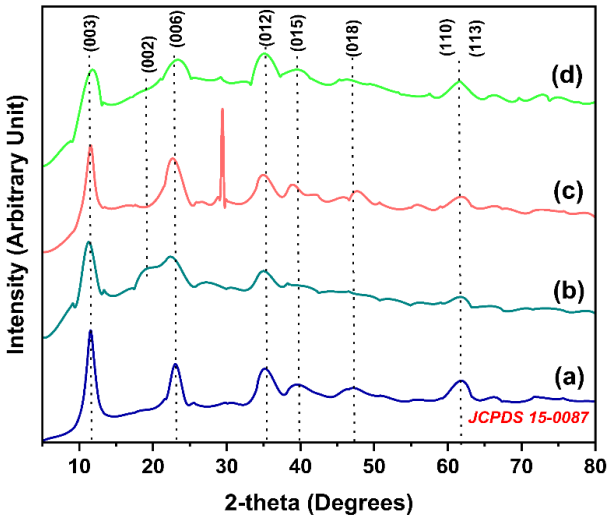

Figure 2. XRD Patterns of Ni/Al-LDH (a), Ni/Al-Ch (b), Ni/Al-Ce (c), and Ni/Al-GO (d)

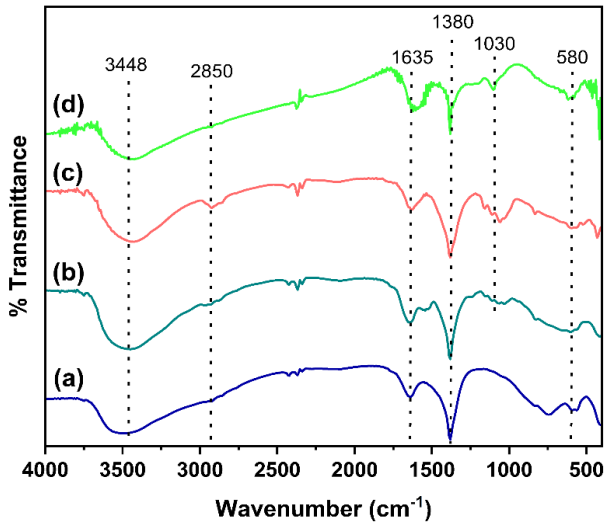

Figure 3. FT-IR Spectra of Ni/Al-LDH (a), Ni/Al-Ch (b), Ni/Al-Ce (c), and Ni/Al-GO (d)

2.6 Material Characterization

A variety of characterization procedures, including XRD, FT-IR, and BET analysis, were performed on the materials that were synthesized. These procedures included the characterization of Ni/Al-LDH, Ni/Al-Ch, Ni/Al-Ce, and Ni/Al-GO. With the intention of determining whether or not the synthesis procedure and the fabrication of the materials in question were successful, this was carried out.

3. RESULTS AND DISCUSSION

The synthesized materials were further analyzed by XRD, FT-IR, and BET surface area to investigate the success of the material synthesis and characterize the material structure. The results of the XRD analysis are shown in Figure 2. XRD analysis was used to characterize the crystalline structure of the synthesized material. As shown in Figure 2(a), Ni/Al-LDH has characteristic diffraction peaks at angles 2θ = 11.6° (003); 23° (006); 35.2° (012); 39.6° (015); 47.4° (018); 61.6° (110); and 62° (113). The resulting diffraction peaks follow JCPDS No. 15-0087 data which is characteristic of diffraction peaks in Ni/Al-LDH materials (Ahmad et al., 2023; Ding et al., 2023). The obvious peak height of Ni/Al-LDH proves the success of the preparation and its high crystallinity.

Figure 2 (a, b, and c) shows the XRD analysis results of Ni/Al-Ch, Ni/Al-Ce, and Ni/Al-GO composite materials, respectively. Based on the XRD pattern, it can be seen that all the characteristic Ni/Al-LDH diffraction peaks are present in the composite material. The broadened diffraction peak around 2θ=18-22° (002) indicates the formation of carbon with an amorph phase obtained from the involvement of carbon-based materials in the composite. According to Tohdee et al. (2024), in the XRD pattern, an identifiable peak at 2θ = 22° indicates the presence of carbon in the material. Thus, the components of both materials (Ni/Al-LDH and carbon-based materials: Ch, Ce, and GO) are present in the composite material, so the material synthesis process was successful. The results of XRD analysis also show that there are changes and shifts in the intensity of the diffraction peaks after Ni/Al-LDH is composited with carbon-based materials, the diffraction peaks in the composite are not higher than the diffraction peaks of pristine Ni/Al-LDH.

FT-IR analysis is shown in Figure 3 which aims to determine the presence of functional groups in the materials. The broad peaks at wave numbers 3448 cm^{-1} and 1635 cm^{-1} are due to the bending vibrations of water molecules (Fu et al., 2022). Vibrations appearing in the region around 3000-2850 cm^{-1} indicate the presence of −CH aliphatic alkanes. Vibrations at 1380 cm^{-1} indicate the presence of NO_3^- ion (Li et al., 2024). This indicates that the interlayer gap added in LDH contains nitrate anion. M−OH stretching (M: Ni & Al) is characterized by the appearance of vibration at 580 cm^{-1} (Radji et al., 2024). In the composite material, there is a vibration in the 1030 cm^{-1} region which indicates the presence of C−O−C groups (Missau et al., 2021), this is produced by the addition of carbon-based materials, namely chitosan, cellulose, and graphene oxide. As shown in Figure 3 (a, b, and c), the functional groups of Ni/Al-LDH are all present in the composite and the addition of functional group components from carbon-based materials. This shows the success of the synthesis process characterized by the combined appearance of the two initial material components in the composite material.

The N_2 adsorption-desorption isotherms are shown in Figure 4. Based on the IUPAC classification, all the materials show type IV hysteresis loop isotherms indicating the materials are classified as mesoporous (Ahmad et al., 2024; Mallakpour et al., 2023). The data also shows the physical characteristics of each material,

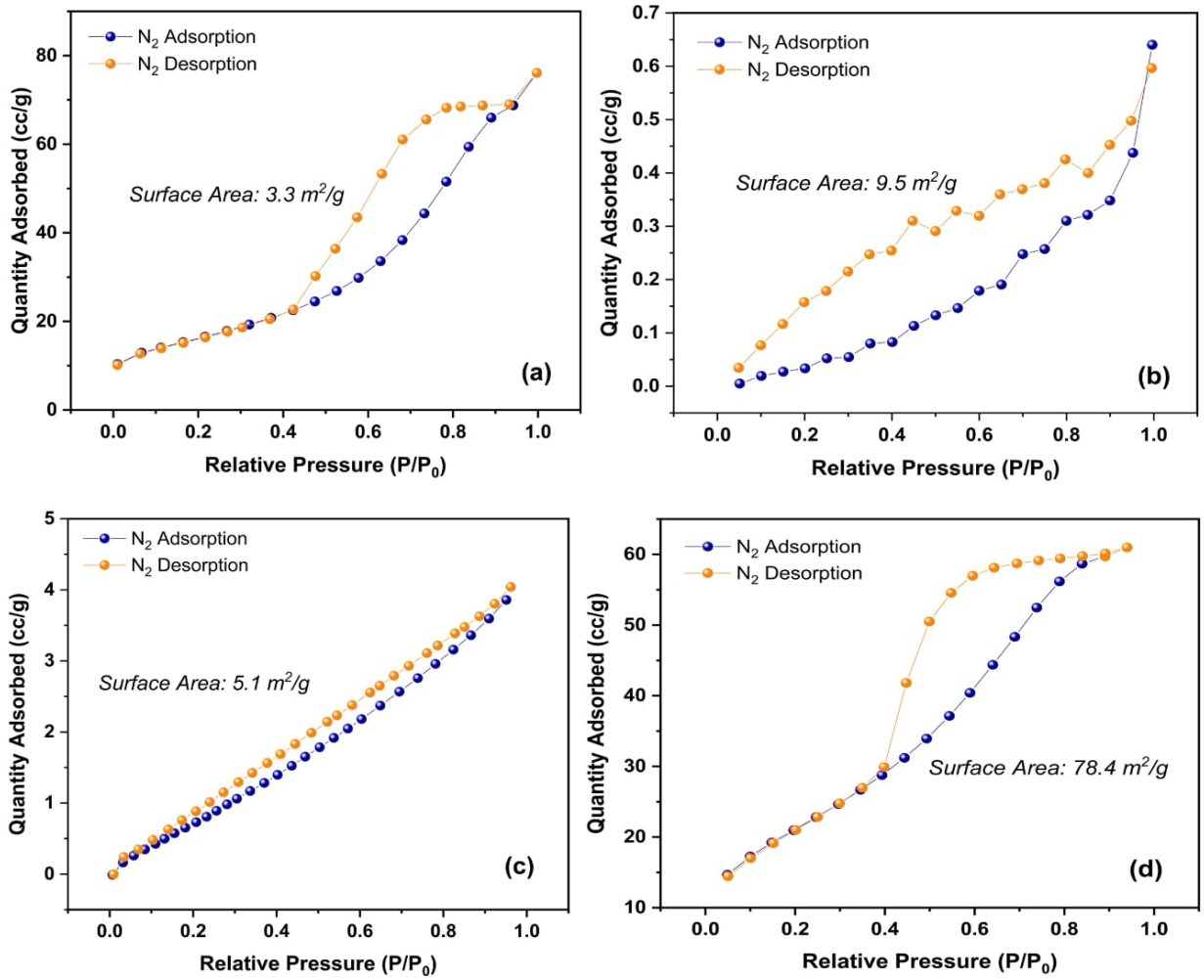

Figure 4. Nitrogen Adsorption-Desorption Isotherms of Ni/Al-LDH (a), Ni/Al-Ch (b), Ni/Al-Ce (c), and Ni/Al-GO (d)

namely surface area. There was an increase in the surface area of the Ni/Al-LDH material after compositing with Ch, Ce, and GO. It can be concluded that the surface area of Ni/Al-GO > Ni/Al-Ch > Ni/Al-Ce. This shows that in this study, the addition of Ch, Ce, and GO materials to Ni/Al-LDH to form a composite will increase the surface area of the material and it proves that the material synthesis was successfully carried out. The well-organized mesoporous structure and large surface area offer more active sites. The increase in surface area is important for material application processes such as photocatalytic/adsorption in terms of allowing pollutants to enter the pores and enhancing electron transfer within them (Feng et al., 2023).

4. CONCLUSIONS

The synthesis process of Ni/Al-LDH composite material has been successfully carried out which is characterized by the combined characteristics of the two starting materials in the composite on XRD and FT-IR analysis. The Ni/Al-LDH material has an increase in surface area after being composited with Ch, Ce, and GO. The surface area of Ni/Al-GO > Ni/Al-Ch > Ni/Al-Ce.

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