

Synthesis and Characterization of Magnetic MgAl-NO₃-HT Composite via the Chemical Co-precipitation Method

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Abstract. Magnetic MgAl-NO₃-Hydrotalcite (MHT) composite was synthesized via a chemical co-precipitation method using sodium hydroxide as the precipitating agent. The synthesized composite was characterized by the Fourier transform infrared spectroscopy (FTIR), the X-ray diffraction (XRD), the scanning electron microscopy (SEM), and Brunauer-Emmett-Teller (BET). The spectra of FTIR indicated that nitrate anion was the interlayer anion for MgAl-NO₃-HT, while the XRD pattern and SEM image showed that magnetite particles were dispersed on the surface of the MgAl-NO₃-HT. This dispersion of magnetite enhanced the specific surface area MgAl-NO₃-HT.

Keywords: Magnetic MgAl-NO₃-Hydrotalcite, chemical co-precipitation, magnetite, composite.

1. Introduction

Magnetic iron oxide nanoparticles have been widely used in various fields such as in magnetic storage media, solar energy transformation, electronics, ferro fluid [1], as well as applied as catalyst [2], drug delivery agent [3], and magnetic adsorbent [4]. Application of magnetic nanoparticles as adsorbent material is driven by the fact that magnetic adsorbent can be easily separated by using an external magnetic field after its utilization [5]. Nanoparticle powders with fine granularity, good dispersion, uniform size and shape are very important in the synthesis of nanoparticle materials. There are several techniques that have been used for the synthesis of magnetic iron oxide nanoparticles, such as co-precipitation which can be used to control particle size.

Mg/Al Hydrotalcite (Mg/Al HT) also known as the Mg/Al Layered Double Hydroxides (Mg/Al LDHs) [6]-[8] is one of the attractive and prospective minerals which is rarely found in nature, but can be easily synthesized through co-precipitation method [6]. Both natural and synthetic, a similar compound hydrotalcite (hydrotalcite-like) having the general formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+} [A^{n-}_{x/n}.mH_2O]^{x-}$, where M²⁺ is a divalent metal such as Mg, Ni, Zn, Cu and M³⁺ is a trivalent metal such as Al, Ga, Cr, Fe and Aⁿ⁻ is an anion of n valence such as CO₃²⁻, OH⁻, Cl⁻, SO₄²⁻ and x value between 0.17 to 0.33 [9]. Chemical co-precipitation method is a method frequently used for the preparation of magnetic Mg/Al HT as it is easy, can be used at low temperatures, efficient and able to produce more products. Mg/Al HT compounds are useful in various applications such as a catalyst, potential material for cleanup and environmental remediation. For cleanup

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and environmental remediation, Mg/Al HT has been widely applied as adsorbent of various anions, such as anionic dye [6], dodecylbenzylsulfonate (DBS) [10] and chromium(VI) [11].

According to Chang, et al (2011) [12], iron oxide nanoparticles can be modified with inorganic compounds like Mg/Al HT to obtain magnetic adsorbent, which as an adsorbent to remove pollutants in the environmental and can be separated again from the adsorbate using external magnetic. Therefore, an inorganic magnetic composite consisted of iron oxide nanoparticles and Mg/Al-NO₃-HT has been synthesized through a chemical co-precipitation method and its characteristic is reported.

2. Material and Method

2.1. Reagents

Analytical grade FeSO₄·7H₂O, FeCl₃·6H₂O, Mg(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, NH₃·H₂O (25%, w/w), NaOH, and HCl were purchased from Merck (Germany). Carbonat-free distilled water was used for preparation of the solution and for rinsing the product.

2.2. Synthesized of magnetite, Fe₃O₄

FeSO₄·7H₂O (6,9503 g) and FeCl₃·6H₂O (10,121 g) were dissolved in 25 ml distilled water. A NH₄OH (3,5 M) solution was added dropwise into the mixed Fe²⁺/Fe³⁺ solution at 50°C under stirring to increase pH until 11. After 3 h aging, the products were separated, washed with distilled water to neutral pH and then dried to obtain magnetite nanoparticles (M).

2.3. Synthesized of Mg/Al-NO₃-HT

A NaOH solution (1.6 M) was added dropwise to a mixed solution of Mg(NO₃)₂·6H₂O (12.8 g, 0.05 mol) and Al(NO₃)₃·9H₂O (9.4 g, 0.025 mol) with stirring in a nitrogen atmosphere at 55 °C. The pH increased by adding NaOH solution to pH value 10. After 1 h aging, the product was hydrothermally processed at 120 °C for 5 h. The white precipitate was separated, washed with water, and dried to obtain Mg/Al-NO₃-HT (HT).

2.4. Synthesized of magnetic Mg/Al-NO₃-HT composite

The Fe₃O₄ powder (0.65 g) was redispersed in distilled water (50 mL). Mg(NO₃)₂·6H₂O (12.8 g, 0.05 mol) and Al(NO₃)₃·9H₂O (9.4 g, 0.025 mol) with Mg²⁺/Al³⁺ molar ratio of 2.0 was dissolved in distilled water (100 mL), and NaOH (6.6 g, 0.165 mol) were dissolved in distilled water (100 mL). The two solutions were added dropwise into the Fe₃O₄ dispersion at 55°C for 1 h under atmospheric nitrogen. After 12 h for aging, the products was hydrothermally at 120°C for 5 h and then separated, washed with distilled water, and then dried to obtain magnetic Mg/Al-NO₃-HT (MHT).

2.5. Characterization of materials

XRD patterns of samples were recorded using a Shimadzu XRD-6000 diffractometer with Ni-filtered Cu K α radiation (λ = 0.15406 nm) at voltage 40 kV and current 30 mA. The sample was scanned in steps of 0.02° (2 θ) in the range from 0 to 70° with a count time of 4 s per step. FT-IR spectra were recorded using a Shimadzu FTIR-820 IPC in the transmission mode in spectroscopic grade KBr pellets for all the powders. The morphology of samples was viewed by scanning electron microscopy (SEM) using a JSM-6360 instrument. Brunauer–Emmett–Teller (BET) surface area was determined by using a Quantachrome Instruments version 11.0.

2.6. Adsorption test of [AuCl₄]⁻

A series of [AuCl₄]⁻ solution (10 ml, 25 ppm) was adjusted to pH 2, 3, 4, 5, 6, 7, and 8 by adding either HCl or NaOH solution. Into every [AuCl₄]⁻ solution, 10 mg of MHT was poured and then shaken for 90 minutes. After that adsorbent particles were separated by external magnet. The concentrations of [AuCl₄]⁻ in the filtrate were analyzed using Atomic Absorption Spectroscopy (Analytic Jena ContrAA 300, λ =242,8 nm).

3. Results And Discussion

3.1. FTIR spectroscopy

FTIR analysis for magnetite is used to identification the functional groups and purity of magnetite while for HT, it is used to get information about the anions present in the interlayer between the brucite-like sheets. FTIR characterization results for magnetic Fe_3O_4 showed the absorption band at 586.36 cm^{-1} which indicates stretching vibration of Fe-O bond (Fig. 1A). Additional, peaks at 1627.92 and 3402.48 cm^{-1} can be attributed to the stretching vibration of the hydroxyl groups on the surface of the magnetite nanoparticles [13]. It can be deduced that on the surface of Fe_3O_4 occur hydrolysis and formed $\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$ and FeOOH [14]. Since the absorption peak at wave number region 3402.43 cm^{-1} is weak indicates that the crystallization of magnetite completed [15].

FTIR spectra HT and MHT appears strong absorption band at wave number 1381.03 cm^{-1} which is the NO_3^- stretching vibration. This shows that the nitrate anion is present between layers of both HT and MHT. [16]-[17]. Weak absorption at wave numbers 1635.64 cm^{-1} shows the -OH vibrations of H_2O on the interlayer and broader the absorption wave number 3471.87 or 3479.58 cm^{-1} shows the -OH stretching vibration of Mg-OH and Al -OH [18]-[19].

3.2. X-ray diffraction

The XRD pattern of Fe_3O_4 , HT and MHT composites is illustrated in Fig 1B. The series of characteristic peaks for Fe_3O_4 are strong peaks located at $2\theta = 30.2^\circ$, 35.6° , 43.3° , 57.1° , and 62.7° that can be assigned to the (220), (311), (400), (511) and (440) reflections. That reflection peaks can be indexed to the inverse spinel structure of Fe_3O_4 . The average size of the particles Fe_3O_4 is to be 17.5 nm which is calculated using the Debye-Scherrer equation [20]. Based on the results of XRD pattern for HT the peaks appear at 2θ : 11.17° , 22.62° , 35.39° , 62.67° . The characteristic peaks of both HT and MHT composites indicate that both of them have a layered structure with basal spacing 7.91 \AA and 8.86 \AA which indicated NO_3^- anion in interlayer [21]. There was suitability with FTIR characterization results. The peak of MHT which correspond to the basal spacing (009) is divided into two sub-peaks. The first one at a smaller diffraction angle shows the peak for HT, whereas the second one at a slightly greater diffraction angle come from the Fe_3O_4 particle core, on the surface of which the HT are deposited [12]. With a sharp peak for Fe_3O_4 (M) and MHT, indicative of obtaining the products have better crystallinity.

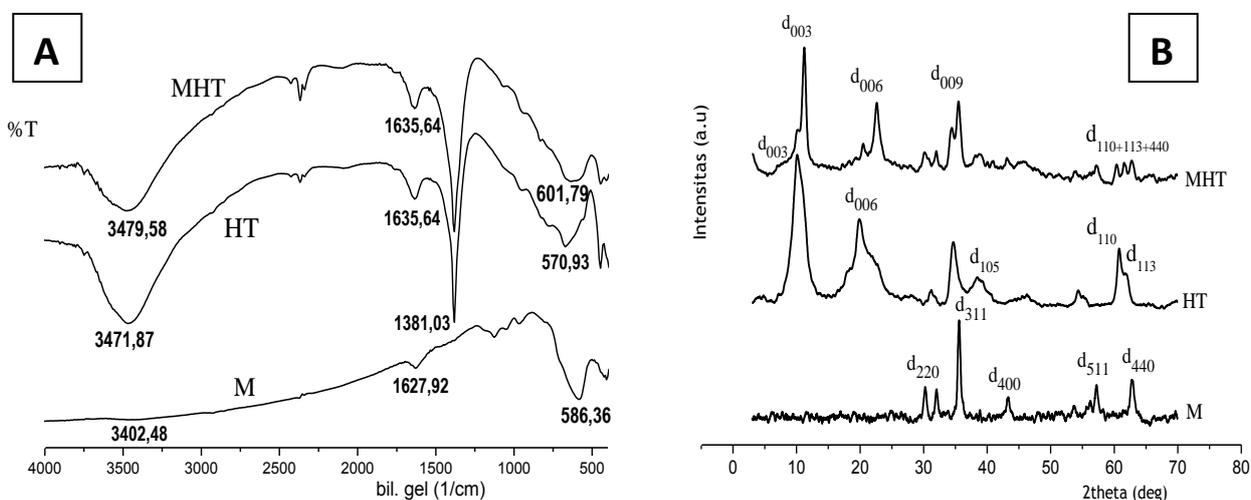


Fig. 1: (A) FTIR Spectra and (B) XRD patterns of Fe_3O_4 (M), HT and MHT.

Table 1: Textural properties of material determined of BET

Sample	SBET (m^2/g)	V _p (cm^3/g)	D _p (nm) BJH method
HT	5.759	0.026	21.702
MHT	67.734	0.340	21.726

3.3. Specific surface area and morfology

MHT has a BET specific surface area larger than HT as well as the pore volume (V_p). This suggests that the incorporation of magnetite particles can greatly expand the surface area of the material. On the other hand, the deposition of magnetite nanoparticles did not significantly affect the pore diameter (D_p) (see Table

1). The pore size distribution of both HT and MHT show that large mesopores (2-30 nm) are formed. Although the largest pore diameter distribution HT and MHT are the same, but the particle size MHT more uniform nano-scale than HT (Fig. 2).

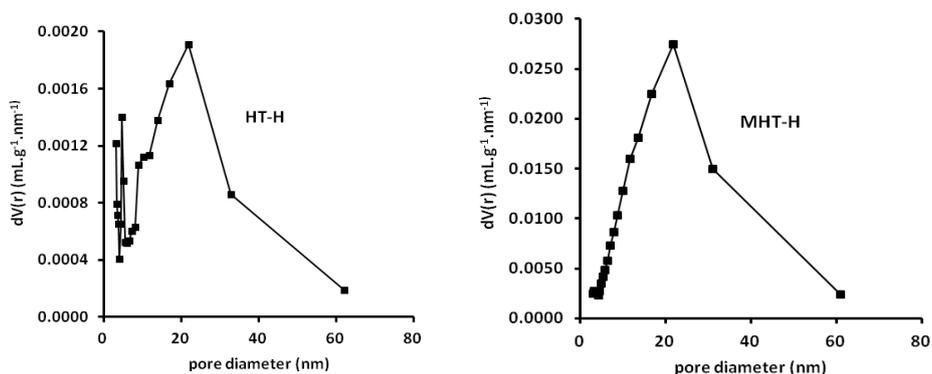


Fig. 2: Pore size distribution of HT and MHT

The spherical shaped nanosize magnetite particles were successfully prepared as shown in Fig. 3. The SEM image of the bare magnetite nanoparticles is shown in Fig. 3a. It has a uniform morphology and the particles tend to agglomerate. As for SEM images of HT and MHT in Fig. 3b and 3c, indicates that the magnetite particles dispersed evenly on the surface HT.

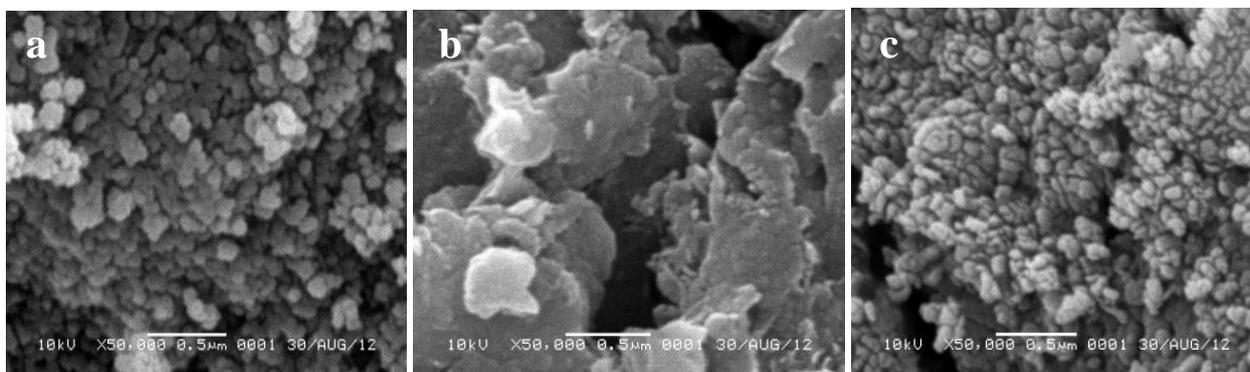


Fig. 3: SEM image of Fe₃O₄ (a), HT (b) and MHT (c)

3.4. Adsorption of [AuCl₄]⁻

MHT composites used to adsorb [AuCl₄]⁻ on media pH varying from 2 to 8. The adsorption of [AuCl₄]⁻ on MHT composite tends to increase with increasing acidity from pH 2 to 3 and then decrease from pH 4 to 8 (Fig. 4). Optimum adsorption occurs at pH 3 with a percentage of adsorption is 90.4 %.

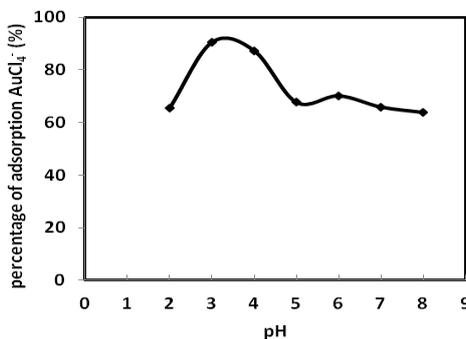


Fig. 4: Effect of pH on the adsorption percentage (the initial [AuCl₄]⁻ concentration was 25.0 mg L⁻¹; adsorbent dose 0.01 g)

4. Conclusion

Chemical co-precipitation method can be used to generate Fe₃O₄ nanoparticles and composite magnetic MgAl-NO₃-HT with high crystallinity and small particle size. The presence of magnetite nanoparticles on the surface of MgAl-NO₃-HT enhanced greatly the specific surface area and affect to the uniformity of pore diameter.

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6. References

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