Natural iron sand-based $\text{Mg}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$ nanoparticles as potential adsorbents for heavy metal removal synthesized by co-precipitation method

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Abstract. Natural iron sand-based $\text{Mg}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$ magnetic nanoparticles ($x = 0.25, 0.50, 0.75$) were synthesized using a simple co-precipitation method. The resulting nanoparticles were characterized by X-Ray Diffraction, Vibrating Sample Magnetometer, Energy Dispersive X-Ray Analysis, Atomic Absorption Spectroscopy and Scanning Electron Microscopy. The crystallite size data of the $\text{Mg}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$ revealed that all samples with varied $x$ lie under 17 nm; with $x = 0.5$ variation having the least crystallite size of 14.90 nm. The surface microstructure elucidation by SEM also confirmed the presence of agglomeration at $x = 0.5$. Optimal condition of magnetic properties was observed in $\text{Mg}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$ ($x = 0.75$), as was displayed by the M-H curves. The adsorption capacity up to 190.5 mg/g implies that $\text{Mg}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$ nanoparticles have the ability to emerge as one of the beneficial adsorbents for the removal of heavy metal ions, mainly Pb and Cu ions.

1. Introduction

Clean water access has become a crucial issue the world encounters for the past few decades. Heavy metal ions (e.g: Pb$^{2+}$, Cu$^{2+}$, Hg$^{2+}$) are the most common water pollutants which can lead to a variety of contaminations and diseases [1,2]. Thus, the removal of heavy metals from natural water sources as well as wastewater streams is becoming increasingly important. One of the accessible solutions to this environmental problem is by applying magnetic adsorbents in form of nanoparticles [3].

Magnetic adsorbents can be used to adsorb contaminants from aqueous or gaseous effluents [4]. The potential adsorbent that has been gaining more interest in recent years is ferrite magnetic nanoparticles (MNPs). Ferrite MNPs are the most explored magnetic nanoparticles and are widely known for their superior magnetic properties and a large variety of applications, including semiconductors [5], low magnetic materials [6], and gas sensing [7]. Apart from these applications, this spinel-type MNPs have a prospective usage in the treatment of an aqueous environment. Additionally, compared to the conventional adsorbents, iron oxide nanoparticles have several advantages. First, they are eco-friendly adsorbents [8]. Second, contaminants can be adsorbed onto nano-sized iron oxides in practically tolerable times [9]. Third, magnetic iron oxide nanoparticles can be comfortably separated from aqueous samples by applying an external magnetic field [10].

Indonesia’s rich natural resources provide a great platform for researchers to develop and process green materials such as iron sand into a more applicable material. Natural iron sand with its high iron...
content makes it an obtainable source for synthesizing ferrite MNPs. There are several techniques to synthesize ferrite nanoparticles; these include ceramic technique [11], hydrothermal [12], co-precipitation [13], and sol-gel [14]. Of these, the co-precipitation method is an effective technique for preparation of ferrites at nanoscale. It is a low-temperature process and provides good control over crystallite size [15].

The present work was one such effort to synthesize Mg$_{1-x}$Ni$_x$Fe$_2$O$_4$ nanoparticles by co-precipitation method and to characterize their physical and magnetic properties. The effects of different compositions of Mg and Ni denoted by three different $x$ values on the formation of nanoparticles were also examined. This study ultimately could give us a better perceptive on the adsorption behavior of Mg$_{1-x}$Ni$_x$Fe$_2$O$_4$ towards heavy metal ions, particularly Pb and Cu ions. We expect Mg$_{1-x}$Ni$_x$Fe$_2$O$_4$ would be a viable alternative for a more efficient magnetic adsorbent material in the years to come.

2. Experimental method

Ni$^{2+}$-substituted magnesium ferrite nanoparticles Mg$_{1-x}$Ni$_x$Fe$_2$O$_4$ ($x = 0.25, 0.50, 0.75$) were prepared using co-precipitation method. The iron content was obtained from the natural iron sand located in the island of Sumatera, Indonesia. Iron sand, MgCl$_2$.6H$_2$O, NiCl$_2$.6H$_2$O, HCl 37% and NH$_4$OH were used as the starting materials. First, MgCl$_2$.6H$_2$O (2.45 g; 1.63 g; 0.81 g for $x = 0.25$; 0.50; 0.75, respectively) and NiCl$_2$.6H$_2$O (1.11 g; 2.23 g; 3.35 g for $x = 0.25$; 0.50; 0.75, respectively) were dissolved in distilled water. Each mixture was blended in a beaker glass until uniform. For the second solution, 8 g of iron sand powder were stirred together with HCl acid until homogenous.

Both starting mixtures were well blended to form a solution which was then added (dropwise) into a 99 ml of 3M NH$_4$OH solution. The reaction was carried out with the use of magnetic stirrer at 500 rpm and 60 °C for 2 hours at a pH of 12. The precipitates formed were filtered and cleansed several times to remove the impurities. The precipitates then were mixed with distilled water in a laboratory centrifuge for 10 minutes at 2500 rpm and oven dried at 50 °C. The final products (in the form of powder) were mixed with an artificial waste solution made from Pb and Cu salt dissolved in water to calculate the adsorption capacity of the nanoparticles.

To analyze the physical, magnetic, and adsorption properties of Mg$_{1-x}$Ni$_x$Fe$_2$O$_4$ nanoparticles, the dried products were characterized by various tools including pycnometer, X-Ray Diffraction Rigaku ($\lambda$=1.5418 Å), Vibrating Sample Magnetometer, Energy Dispersive X-Ray Analysis, Scanning Electron Microscopy (Hitachi 3500 SU), and Atomic Absorption Spectroscopy (Shimadzu AA6800).

3. Results and discussion

The XRD diffraction peaks of Mg$_{1-x}$Ni$_x$Fe$_2$O$_4$ nanoparticles are presented in Figure 1. All samples were confirmed to have cubic crystal structure which is a common structure for spinel-type MNPs. As shown in the figure, at $x = 0.50$, the Mg$_{1-x}$Ni$_x$Fe$_2$O$_4$ had a peculiar peak marked with an asterisk. This peak was identified as an impurity phase of hematite ($\alpha$-Fe$_2$O$_3$) which occurred due to the remaining unreacted Fe$^{3+}$ ions. Further analysis on the XRD characterization display several other parameters, namely crystallite size, powder density, and lattice parameter; all of which can be seen in Table 1.

| x   | $\rho$ (g/cm$^3$) | a (Å) | D (nm) | $H_c$ (Oe) | $M_s$ (emu/g) | $M_R$ (emu/g) |
|-----|------------------|-------|--------|------------|---------------|---------------|
| 0.25 | 3.94             | 8.39  | 15.45  | 37.70      | 55.23         | 1.58          |
| 0.50 | 4.07             | 8.38  | 14.90  | 28.66      | 52.37         | 3.68          |
| 0.75 | 3.87             | 8.38  | 16.68  | 45.93      | 54.56         | 3.42          |
Figure 1. X-ray diffraction patterns of Mg$_{1-x}$Ni$_x$Fe$_2$O$_4$ nanoparticles with different x values. (a) x = 0.25, (b) x = 0.50, and (c) x = 0.75, respectively. The peak labeled as an asterisk arise from the hematite phase.

The crystallite size of Mg$_{1-x}$Ni$_x$Fe$_2$O$_4$ was calculated from X-ray diffraction line broadening using Scherrer’s formula in Eq. (1) [16].

$$D = \frac{k \cdot \lambda}{\beta \cdot \cos(\theta/2)}$$  

(1)

Where D is the crystallite size, K is the Scherrer constant, $\lambda$ is the wavelength of X-ray beam used (1.5418 Å), $\beta$ is the full-width half maximum of diffraction and $\theta$ is the Bragg’s angle.

From the data exhibited in Table 1, it appears that Mg$_{1-x}$Ni$_x$Fe$_2$O$_4$ with x = 0.50 had the smallest crystallite size of 14.90 nm and possessed the highest powder density of 4.07 g/cm$^3$ despite the occurrence of the hematite impurity phase. It is noticed that the lattice parameters for all x values are rather similar, approximately around 8.3 Å which would validate the existing structure of this spinel-type MNPs as cubic structure. To capture a better glimpse of the nanostructure, we investigated the morphology of this sample (x = 0.50) using SEM which will be discussed later on.

Figure 2. Hysteresis curves of Mg$_{1-x}$Ni$_x$Fe$_2$O$_4$ nanoparticles. The optimal condition occurs when x = 0.75 (shown by an arrow).

The magnetization hysteresis loops of three different x values are shown in Figure 2. The M–H curve of x = 0.75 (denoted with a blue line) has a distinct feature of maximal magnetic curve as exposed in details in Table 1. The magnetic properties presented are coercivity, saturation, and remanence. We can clearly see that at x = 0.75, Mg$_{1-x}$Ni$_x$Fe$_2$O$_4$ nanoparticles demonstrated an optimal condition of magnetic properties, with magnetic coercivity and saturation values reached as high as 45.93 Oe and 54.56 emu/g,
respectively. This indicates that as the crystallite size increased, the coercivity and saturation values were also enhanced significantly. This feature could be resulted from various aspects, such as the composition, crystallinity, size, and phases [17].

![SEM Image](image)

**Figure 3.** (a) SEM image of Mg$_{1-x}$Ni$_x$Fe$_2$O$_4$ (x = 0.50) nanoparticles.

Figure 3 presents a typical SEM photograph of the nanoparticles (x=0.50). It seemed that the particles of Mg$_{1-x}$Ni$_x$Fe$_2$O$_4$ in Figure 3 had a tendency to agglomerate, which might occur due to the hematite impurity phase shown in Figure 1. This sort of unstable trait is commonly found in ferrite based magnetic nanoparticles [18]. A further morphological examination with TEM would provide us with a more integrated analysis on the structure, hence a more lucid analysis.

| x   | Concentration of Pb and Cu ions (ppm) | Adsorption capacity (mg/g) |
|-----|--------------------------------------|---------------------------|
|     | Initial 1092                         | Final 711                |
| 0.25|                                      | 190.5                    |
| 0.50|                                      | 158                      |
| 0.75|                                      | 187.5                    |

**Table 2.** Adsorbent properties of Mg$_{1-x}$Ni$_x$Fe$_2$O$_4$ nanoparticles on Pb and Cu ions with varying x values.

From the EDX spectra (not shown here), we could also attain several elements which mainly contained Fe (59 wt.%) and O (32 wt.%), while Mg (7 wt.%) and Ni (2 wt.%) were the elements with the lowest amount of wt.%. Atomic Absorption Spectroscopy (AAS) analysis was conducted to retrieve adsorption capacity and removal efficiency values of the samples towards Pb and Cu ions, as listed in Table 2. From the table, we can conclude that Mg$_{1-x}$Ni$_x$Fe$_2$O$_4$ at x = 0.25 had the highest adsorption capacity (190.5 mg/g), hence the largest removal efficiency of 34.89 %. The low percentage stated here infers that the higher concentration of both Pb and Cu ions of around 1092 ppm affected the overall removal efficiency outcome. Both Pb and Cu ions initial concentration used in this report was much higher than the one used in our previous work [19]. There, with a much smaller amount of Pb ions (294 ppm), the adsorption capacity only reached up to 143.07 mg/g, yet produced a very high percentage of removal efficiency of 97 % [19]. This suggests that Mg$_{1-x}$Ni$_x$Fe$_2$O$_4$ was able to act as an acceptable adsorbent for both Pb and Cu ions. It is worth noting that this result still offers probability in developing spinel ferrite MNPs as adsorbents for heavy metal ions.
4. Conclusions
The co-precipitation method is quite suitable for the synthesis of Mg$_{1-x}$Ni$_x$Fe$_2$O$_4$. The cubic structure was identified from the XRD details which verify the final product as Mg$_{1-x}$Ni$_x$Fe$_2$O$_4$. The SEM image indicates the formation of agglomerates due to magnetic nature. Further investigation is required to control the agglomeration presents here. The VSM result points out that Mg$_{1-x}$Ni$_x$Fe$_2$O$_4$ nanoparticles with $x = 0.5$ produce minimal magnetic properties, while Mg$_{1-x}$Ni$_x$Fe$_2$O$_4$ nanoparticles with $x = 0.75$ show the opposite outcome of utmost magnetic properties. The removal efficiency analysis on Pb and Cu ions has shown that Mg$_{1-x}$Ni$_x$Fe$_2$O$_4$ nanoparticles with $x$ variation of 0.25 are able to reach an optimal condition with the adsorption capacity of 190.5 mg/g. This approach opens up possibilities of further development of ferrite nanoparticles adsorbent and feasibly a chance for larger scale production of improved adsorbent materials.

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