Methyl orange dye removal using Ni/Fe-NO$_3$ and Ni/Fe-$[$α-SiW$_{12}$O$_{40}$] layered double hydroxides

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Abstract. The material of layered double hydroxide (LDH) Ni/Fe-NO$_3$ was prepared by coprecipitation method under basic condition. Ni/Fe LDH was modified by intercalation using K$_4$[$α$-SiW$_{12}$O$_{40}$] to form Ni/Fe-$[$α-SiW$_{12}$O$_{40}$]$. All materials were characterized by X-ray and FTIR spectroscopy. Ni/Fe LDH and intercalated Ni/Fe LDH were used as adsorbent of methyl orange dye from the aqueous solution. The parameter of adsorption such as kinetic and also thermodynamic adsorption of methyl orange on LDHs were investigated. X-Ray analysis showed that the diffraction at 11.53° [003] of Ni/Fe-NO$_3$ has interlayer distance 7.67 Å shift to 8.20° [003] of Ni/Fe-$[$α-SiW$_{12}$O$_{40}$]$]. FTIR spectra of Ni/Fe-NO$_3$ and Ni/Fe-$[$α-SiW$_{12}$O$_{40}$]$]$ show the wavenumber at 1600 cm$^{-1}$ due to vibration of LDHs anion. Adsorption of methyl orange onto Ni/Fe-NO$_3$ and Ni/Fe-$[$α-SiW$_{12}$O$_{40}$]$]$ follow the pseudo second-order kinetic model, where intercalated material has a higher reactivity than Ni/Fe-NO$_3$ before intercalation. Isotherm model Freundlich was more fitted than isotherm Langmuir for the adsorption of methyl orange on LDHs with multilayer physical adsorption process. Adsorption capacity of methyl orange on Ni/Fe-$[$α-SiW$_{12}$O$_{40}$]$]$ as adsorbent was slightly higher (up to 7.226 mg.g$^{-1}$) than Ni/Fe-NO$_3$ as adsorbent (3.190 mg.g$^{-1}$).

Keywords: Layered double hydroxide, Ni/Fe, K$_4$[$α$-SiW$_{12}$O$_{40}$]$], methyl orange, adsorption

1. Introduction
The research of dyes treatment from wastewater has been conducted until this decade. Various procedures have been used to eliminate dyes from wastewater, namely coagulation [1], filtration [2], and also adsorption [3]. Adsorption is a reliable method due to the high efficiency, simple, and ease of operation. The successful adsorption process depends on properties of adsorbent. Wide range of adsorbents have been synthesized to remove dyes from wastewater such as bentonite [4], kaolinite [5], zeolite [6], and also layered double hydroxide [7]. Layered double hydroxide (LDH) is anionic layered structure material, which has empirical common formula of $[$M$^{2+}(1-x)$M$^{3+}x$(OH)$_2$]$][A$^{m+}$]x/nH$_2$O. LDH
has positively charged and exchangeable anion in the interlayer [8]. The structure of LDH has a unique structure due to anion exchange properties to form selective structure for application of LDH. However, the distance of basal spacing of layered materials still has small interlayer constraints and narrow layer spacing due to the small exchange ions such as nitrate, carbonate, sulfate, and chloride thus layered double hydroxides need to be modified to increase its interlayer distance [9].

Adsorption of congo red dye from aqueous solution was conducted using Mg-Al-layered double hydroxide as adsorbent. The adsorption process was controlled mainly by electrostatic interaction [10]. Anionic dye such as congo red was also removed by Mg-Fe-CO3 as adsorbent by reusing the adsorbent of Mg-Fe-CO3 layered double hydroxide for several times [11]. The adsorption of methyl orange, which is an anionic dye was also carried out using Mg-Al layered double hydroxide as adsorbent with 3D structure with high adsorption capacity [12]. Intercalated layered double hydroxide with heteropoly blue compound [PW10Mo2O40]5- showed an ability for cationic dye removal such as methylene blue [13]. The intercalated layered double hydroxide showed a higher adsorption capacity of methylene blue than the pure layered double hydroxide. Thus, the research of intercalated layer double hydroxide with polyoxometalate is an interesting topic for removal of dyes from aqueous solution.

In this research, Ni/Fe-NO3 was intercalated with Keggin ion [α-SiW12O40]3- to form Ni/Fe-[α-SiW12O40] LDH. Keggin ion is used due to the stability of this polyoxometalate and easy to synthesize in acid aqueous medium. Materials were characterized using X-ray and FTIR analyses. The pHpzc of materials were also identified. Then, materials were used as adsorbent of methyl orange from aqueous solution. Factors that influence the adsorption process such as adsorption time, concentration of methyl orange, and adsorption temperature were studied in this research to obtain the kinetic and thermodynamic parameters of adsorption.

2. Materials and method

2.1. Chemicals and instrumentation

Chemicals were supplied from Merck and Sigma Aldrich as follows nickel(II) nitrate, iron(III) nitrate, sodium tungsten, sodium carbonate, sodium metasilicate, hydrochloric acid, and sodium chloride. Keggin ion of [α-SiW12O40]3- was synthesized according to the literature [XX]. Water was supplied from Research Center of Inorganic Materials and Coordination Complexes, Universitas Sriwijaya. X-ray analysis was measured by Rigaku Miniflex-600 X-ray powder diffraction. Sample was scanned at scan speed 1 deg min-1. FTIR spectra were obtained using Shimadzu FTIR Prestige-21 and spectra were recorded at wavenumber 400–4000 cm-1. Analysis of methyl orange dye was performed using UV-Vis BioBase BK-UV 1800 PC spectrophotometer.

2.2. Synthesis of material Ni/Fe-NO3 and Ni/Fe-[α-SiW12O40]

Synthesis of Ni/Fe-NO3 LDH was conducted using coprecipitation method according to Yang et al. [14] with slight modification. Nickel(II) nitrate was dissolved with water to form 0.3 M Ni(NO3)2. Solution of nickel nitrate was mixed with solution of iron(III) nitrate 0.1 M to form solution A. Sodium hydroxide 2 M was mixed with solution of sodium carbonate 1 M to form solution B. Solution A was mixed with solution B by slowly stirring at room temperature. The solution mixture was adjusted to pH 10–11 by the addition of sodium hydroxide solution. The solid material was formed under constant stirring. Solid material was dried for 24 h to obtain Ni/Fe-NO3 LDH. Material Ni/Fe-NO3 LDH was intercalated with Keggin ion to form Ni/Fe-[α-SiW12O40] using ion exchange method. Compound K4[α-SiW12O40] was dissolved with water (solution A). Ni/Fe-NO3 LDH was mixed with solution of sodium hydroxide (solution B). The solution was introduced with nitrogen gas then the solution A was mixed with solution B under nitrogen condition. The temperature of mixture was adjusted at 40 °C for 24 h to obtain solid material of Ni/Fe-[α-SiW12O40].
2.3. pH point zero charge (pzc) and adsorption experiments

Analysis of pHpzc was conducted using aqueous solution of sodium hydroxide or hydrochloric acid. A series of solution sodium chloride was adjusted to pH 1–10 using aqueous solution of sodium hydroxide or aqueous solution of hydrochloric acid. Then, LDH was added to the solution series. The solutions series was stirred for 24 h. The solution’s pH after filtration was determined using pH meter. pHpzc graph was created by plotting the initial versus final pH.

The adsorption of methyl orange was performed under pHpzc using Ni/Fe-NO₃ and Ni/Fe-[α-SiW₁₂O₄₀] as adsorbents. Adsorption was studied by investigation of adsorption time, initial concentration of methyl orange and adsorption temperature. Adsorption time was varied at 5–120 min. Concentration of methyl orange was varied from 10–30 mg L⁻¹ at temperature 35, 40, 45 and 50 °C.

3. Results and discussion

Materials Ni/Fe-NO₃ and Ni/Fe-[α-SiW₁₂O₄₀] LDHs were analyzed using X-ray analysis and the patterns are shown in figure 1. Material Ni/Fe-NO₃ has diffraction pattern at 11.53° (003), 23.06° (006), 34.83° (012), 39.70° (015) and 60.54° (110) [15]. The formation of well-ordered layer material was identified at 11.53° (003) resulting the interlayer distance of 7.67Å. Material Ni/Fe-NO₃ was intercalated with anion [α-SiW₁₂O₄₀]⁴⁻ to form Ni/Fe-[α-SiW₁₂O₄₀]. Ni/Fe-[α-SiW₁₂O₄₀] has the diffraction pattern at 8.20° (003), 11°, 15–20°, 22–25°, 35–40° and 59–60°. Diffraction at (003) was shifted to a lower angle due to the insertion of Keggin ion. Interlayer distance at 8.20° (003) was 10.78 Å. The interlayer distance after intercalation was increased to 3.11 Å.

The Ni/Fe-NO₃ and Ni/Fe-[α-SiW₁₂O₄₀] LDH FTIR spectra are shown in figure 2a and figure 2b. Material Ni/Fe-NO₃ has vibration at 3400 cm⁻¹ (v OH), 1700 cm⁻¹ (v OH) and 1300 cm⁻¹ [16]. The unique vibration at 1300 cm⁻¹ was assigned to nitrate vibration. Nitrate ion was located on the interlayer distance on LDH. Intercalated material Ni/Fe-[α-SiW₁₂O₄₀] has similar main vibrations with Ni/Fe-NO₃. The intensity of vibration at 1300 cm⁻¹ was decreased due to the insertion of Keggin ion [α-SiW₁₂O₄₀]⁴⁻ on interlayer Ni/Fe LDH. Vibrations at 700–900, 1100 cm⁻¹ on Ni/Fe-[α-SiW₁₂O₄₀] were attributed to W-O-W, W=O, and Si-O vibrations of Keggin ion.

Figure 3 shows that intersection point of Ni/Fe-NO₃ LDH was at 7 while Ni/Fe-[α-SiW₁₂O₄₀] at 9. There is no charges at that intersection point and charges of materials were zero. pHpzc below the intersection point is dominated by proton and material with positive charge. On the other hand, negative charge was dominated at above intersection point of pHpzc due to hydroxyl ion form solution. Adsorption of methyl orange on Ni/Fe-NO₃ and Ni/Fe-[α-SiW₁₂O₄₀] LDHs was conducted at pHpzc.

Figure 1. XRD powder pattern of Ni/Fe-NO₃ (a) and Ni/Fe-[α-SiW₁₂O₄₀] (b) LDHs.
Adsorption of methyl orange on Ni/Fe-NO₃ and Ni/Fe-[α-SiW₁₂O₄₀ ] LDHs was studied by investigating the adsorption time, concentration of methyl orange and adsorption temperature. Effect of adsorption time of congo red on both Ni/Fe-NO₃ and Ni/Fe-[α-SiW₁₂O₄₀ ] LDHs is shown in figure 4.

Figure 2. FTIR spectra of Ni/Fe-NO₃ (a) and Ni/Fe-[α-SiW₁₂O₄₀ ] (b) LDHs.

Figure 3. pHpzc graph of initial pH (a), Ni/Fe-NO₃ (b, ) and Ni/Fe-[α-SiW₁₂O₄₀ ] (c) LDHs.

Figure 4. Effect adsorption time of Ni/Fe-NO₃ (a) Ni/Fe-[α-SiW₁₂O₄₀ ] and (b) LDHs.
Adsorption of methyl orange for both LDHs increases with the increase of adsorption time and reached the equilibrium at 70 min for both LDHs. The pattern of methyl orange adsorption on both LDHs was similar but the amount of adsorption was different. The adsorbent Ni/Fe-[α-SiW12O40] has a higher adsorption amount than Ni/Fe-NO3. Data of adsorption time in figure 4 was processed using the pseudo first and second order kinetic models to obtain kinetic adsorption rate for methyl orange on LDH [17].

The data of kinetic model as shown in table 1 showed that methyl orange was adsorbed on both of Ni/Fe-NO3 and Ni/Fe-[α-SiW12O40] LDHs by following the pseudo second-order kinetic model. Adsorption rate for Ni/Fe-[α-SiW12O40] was faster than Ni/Fe-NO3 thus, the adsorbent Ni/Fe-[α-SiW12O40] has a higher reactivity than adsorbent Ni/Fe-NO3.

The effect of methyl orange concentration and temperature adsorption on Ni/Fe-NO3 and Ni/Fe-[α-SiW12O40] LDHs is shown in figure 5. Adsorption of methyl orange was increased with the increase of methyl orange concentration for both LDHs. The increase adsorption temperature was also increasing the adsorption amount of methyl orange. The data in figure 5 showed that adsorption of methyl orange on LDHs was a multilayer process, which was indicated at concentration 20 mg L⁻¹ for both LDHs. Thermodynamic adsorption parameter of methyl orange can be obtained using the data in figure 5, which was calculated using thermodynamic equation [18]. The thermodynamic data is presented in table 2.

The data in table 2 showed the value of adsorption capacity, Gibbs energy, enthalpy, and entropy of methyl orange adsorption on LDHs. The adsorption capacity of methyl orange for both adsorbents in the range 3.190–7.226 mg g⁻¹ showed an increase of adsorption capacity after intercalated Ni/Fe-NO3.

### Table 1. Kinetic model of methyl orange adsorption.

| Kinetic model                      | Value | Adsorbent          |
|------------------------------------|-------|--------------------|
| Pseudo first-order kinetic model   | Qe exp (mg g⁻¹) | Ni/Fe 2.086 Ni/Fe-[α-SiW12O40] 2.686 |
|                                    | Qe calc (mg g⁻¹) | Ni/Fe 1.633 Ni/Fe-[α-SiW12O40] 1.774 |
|                                    | R²     | Ni/Fe 0.429 Ni/Fe-[α-SiW12O40] 0.446 |
| Pseudo second-order kinetic model  | Qe exp (mg g⁻¹) | Ni/Fe 2.086 Ni/Fe-[α-SiW12O40] 2.686 |
|                                    | Qe calc (mg g⁻¹) | Ni/Fe 0.008 Ni/Fe-[α-SiW12O40] 0.017 |
|                                    | R²     | Ni/Fe 0.831 Ni/Fe-[α-SiW12O40] 0.964 |

![Figure 5. Effect of methyl orange concentration and temperature adsorption on Ni/Fe-NO3 (a) Ni/Fe-[α-SiW12O40] and (b) LDHs.](image)
Table 2. Thermodynamic adsorption parameter of methyl orange on LDH.

| LDHs          | T (°C) | Qe (mg g⁻¹) | ΔG° (kJ mol⁻¹) | ΔH° (kJ mol⁻¹) | ΔS° (J mol⁻¹ K⁻¹) |
|---------------|--------|-------------|----------------|----------------|--------------------|
| Ni/Fe-NO₃     |        |             |                |                |                    |
| 35            | 3.190  | -20.693     |                |                |                    |
| 40            | 3.564  | -21.055     |                |                |                    |
| 45            | 3.826  | -21.391     |                |                |                    |
| 50            | 4.256  | -21.728     |                |                |                    |
| Ni/Fe-[α-SiW₁₂O₄₀] |        |             |                |                |                    |
| 35            | 4.256  | -47.117     |                |                |                    |
| 40            | 5.221  | -47.934     |                |                |                    |
| 45            | 6.169  | -48.700     |                |                |                    |
| 50            | 7.226  | -49.465     |                |                |                    |

to Ni/Fe-[α-SiW₁₂O₄₀]. All adsorption of methyl orange on LDHs was spontaneously occurred due to the negative value of Gibbs energy. Adsorption of methyl orange on LDH was classified as physical adsorption with energy in the range 25.707–50.998 kJ mol⁻¹ and also there was a randomness increase of adsorption system on Ni/Fe-[α-SiW₁₂O₄₀] as adsorbent.

4. Conclusion

Adsorption of methyl orange on Ni/Fe-NO₃ and Ni/Fe-[α-SiW₁₂O₄₀] follows the kinetic pseudo-second-order model with high reactivity of Ni/Fe-[α-SiW₁₂O₄₀]. Adsorption capacity of methyl orange on Ni/Fe-[α-SiW₁₂O₄₀] (up to 7.226 mg g⁻¹) was higher than Ni/Fe-NO₃ (up to 4.256 mg g⁻¹) and adsorption was categorized as physical adsorption with the energy range of 25.707–50.998 kJ mol⁻¹. The adsorption process was spontaneously occurred by the increase of randomness system from Ni/Fe-NO₃ to Ni/Fe-[α-SiW₁₂O₄₀].

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