



Synthesis of NiAl-Layered Double Oxide as Inorganic Adsorbent for Eliminating Dye from Solution

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Abstract

The formation of inorganic adsorbent, nickel/aluminium-layered double oxide prepared by calcining nickel/aluminium-layered double hydroxide at 400 °C for 120 min using as dye adsorbent, was verified by XRD pattern, SEM image, as well as FTIR and UV-visible spectra. The calcined product showed higher removal efficiency than that of the uncalcined one resulting from larger surface area and pore volume, and memory effect. The different charge of dye molecules was an important factor on the adsorption of the calcined adsorbent where orange II and methyl orange with negative-charged molecule were eliminated more in comparison with neutral and cationic dye molecules, according to the chemical adsorption due to the electrostatic interaction. The amount of orange II was removed more than that of methyl orange as a result of the structural affinity on reconstruction of layered double hydroxide with host-guest interaction.

Keywords: dye removal, layered double oxide, adsorbent, layered double hydroxide

Introduction

Nowadays, the colorful products are clearly seen almost every place that composed of many organic dye species, besides the demand for both goods and dye stuffs tends to rise continuously. As a result, the unwanted amount of chemical dye or dye effluent is increased and then discharged undeniably into environment especially water resource causing wastewater (Ahmad et al., 2015; Kausar et al., 2018). Even tiny amount of the pollutant contaminated in water has still been highly harmful on ecosystem and living conditions, and then circulated to human health due to highly structural resistance on bio and chemical degradation, therefore, remediation of the toxic dye molecules should be emergently proceeded (Kausar et al., 2018; Yang, Li, Li & Yan, 2018). Such wastewater purification processes as coagulation, flocculation, electrochemical strategy, photocatalysis and biodegradation show potential for eliminating dye effluents from water and/or solution but those are complex that must have expert and experience, special materials and high-cost process (Qiu et al., 2015; Wang et al., 2018). One of them, adsorption strategy is considered due to efficient method, available technique for versatile removal of toxic species and practical, as well as easy preparation and modification of the adsorbent with high adsorption capability and reusability.

Layered double hydroxide, abbreviated as LDH, a class of anionic clay family, has intensively investigated as adsorbent and the others, for instance; catalysts, catalyst support, biological and medical agents, stabilizer and host or support material for controlling particle size (Sun, Zhou, Cai, Zhao & Yuan, 2015; Khumchoo, Khaorapong, Ontam, Intachai & Ogawa, 2016). Many considerations are large surface area, interlayer ion exchangeability feasible for various guest species, swelling ability, positive-charge surface and synergistic behavior of catalyst (Cai et al., 2019). The outstanding features come from the unique structure of the LDH



with typical formula $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n}\cdot m\text{H}_2\text{O}$ where M^{2+} and M^{3+} are di- and trivalent cations, and A^{n-} is a charge compensating inorganic or organic anion in the interlayer space such as NiAl-LDH (Sun et al., 2015), CoAl-LDH (Qiu et al., 2015), NiFe-LDH (Wang, Xiang, & Li, 2010) and so forth. Here, NiAl-LDH was used as adsorbent, and precursor for transforming into another form of smart material by calcination treatment because of its advantages on high adsorption efficiency, high structural stability, and low toxicity promoting economic and environmental benefits for wastewater purification, as well as easy preparation via hydrothermal reaction through urea hydrolysis. By calcination at finite temperature, LDH can be easily turned into layered double oxide (abbreviated as LDO) under four steps due to evaporation of water molecule, dehydroxylation, decomposition of the intercalated anion species and oxide segregation, respectively (Zou et al., 2016). The electronic structure and physicochemical features of LDO have been studied so far, as well as various properties are also reported with potential adsorption of heavy metal and organic species, catalyst and catalyst support. Also, LDO can simply re-established lamellar structure in the presence of the compensated anion in basic solution, which called memory effect (Gao et al., 2016; Bai, Hu, Liu & Qu, 2019). Namely, the adsorption of anionic species on the surface of LDOs with the electrostatic interaction can generate the LDH structure again by which the anions are intercalated and counterbalanced (Lv et al., 2018). As far as we know, the removal of four dye species containing different charge from solution using NiAl-LDO prepared by calcination treatment of NiAl-LDH as the adsorbent is the first report.

Various dye molecules, rhodamine 6G, phenolphthalein, methyl orange and orange II are used as the representative of dye pollutants as these dye species are mostly used and remained in water resource. In this work, hydrothermal method was used to prepare NiAl-LDH as the precursor to achieve NiAl-LDO adsorbent, and the capacity of the LDO on removing the pollutants from solution was investigated in comparison with NiAl-LDH adsorbent.

Materials and Methods

Chemicals

Hydrated salts of nickel chloride ($\text{NiCl}_2\cdot 6\text{H}_2\text{O}$) and aluminium chloride ($\text{AlCl}_3\cdot 6\text{H}_2\text{O}$) were purchased from Carlo Erba Reagenti. Urea ($(\text{NH}_2)_2\text{CO}$) was purchased from Asia Pacific Specialty Chemicals LTD. Rhodamine 6G ($\text{C}_{28}\text{H}_{31}\text{N}_2\text{O}_3\text{Cl}$), phenolphthalein ($\text{C}_{20}\text{H}_{14}\text{O}_4$), methyl orange ($\text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S}$) and orange II ($\text{C}_{16}\text{H}_{11}\text{N}_2\text{NaO}_4\text{S}$) were purchased from Acros. All chemicals are the reagent grade and were used directly without any further purification.

Preparation of the inorganic adsorbent

NiAl-LDH intercalated with carbonate was prepared by hydrothermal conditions using urea decomposition to ammonia. Typically, an aqueous solution of 0.10M NiCl_2 (1.9015 g), an aqueous solution of 0.05M AlCl_3 (0.9657 g) and an aqueous solution of 0.35M urea (1.6817 g) with total volume of 80 mL were mixed under magnetic stirring at room temperature for 10 min, and subsequently was poured into a Teflon-lined autoclave, and then allowed the hydrothermal reaction at 150 °C for 48 h. The obtained precipitate was collected by centrifugation, washed several times with DI water and then ethanol, finally dried at 60 °C for 24 h to obtain NiAl-LDH powder and used as the precursor for preparation of layered double oxide. NiAl-LDO adsorbent was carried out by calcining the as-prepared LDH powder with appropriate amount of in air at 400 °C for 120

min. The conditions (400 °C and 2 h) of calcination treatment were optimized with the resulting large surface area, and cost and time saving advantages.

Characterization

Powder X-ray diffraction (XRD) patterns of the products were collected on a Bruker D8 ADVANCE diffractometer using monochromatic CuK α radiation ($\lambda = 1.5418 \text{ \AA}$). Fourier transformed infrared (FTIR) spectra of the powder samples were recorded on a Perkin Elmer Spectrum One FT-IR spectrophotometer by KBr disk method. Scanning electron microscope (SEM) images of the products were measured on a LEO-1450VP. Nitrogen adsorption/desorption isotherms of the adsorbents were obtained using a Micromeritics ASAP 2010 equipment after the sample was degassed at 150 °C under vacuum for 3 h, and specific surface area of all samples was determined using the Brunauer Emmett-Teller (BET) method. Diffuse reflectance absorption spectra of the solid samples were recorded on a Shimadzu UV-VIS-NIR3101PC scanning spectrophotometer in the range of 200–800 nm using an integrated sphere. UV-visible absorption spectra of the supernatant solution of dye were conducted in the wavelength range of 200–800 nm using a Shimadzu UV-1700 Pharmaspec UV-VIS spectrophotometer.

Dye removal by adsorption method

The adsorption reaction of various dye (rhodamine 6G, phenolphthalein, methyl orange and orange II, Figure 1) solution was performed using NiAl-LDO and NiAl-LDH as the adsorbent by adding 15 mg of the adsorbent in the solution of dye under magnetic stirring at room temperature in the dark area. 20 ppm concentration of dye solution was prepared by dissolving the appropriate amount of dye powder in aqueous solution, except for phenolphthalein that dissolved by mixture solution of DI water and ethanol (1:1 V/V), and 50 mL of the resulting mixture solution was used for each batch. The adsorption process was carried out under solution pH of rhodamine 6G, phenolphthalein, methyl orange and orange II about 6.6, 6.8, 5.4 and 4.6, respectively. To determine the removal efficiency of the inorganic adsorbent for eliminating dye molecules from solution followed as eq. 1, the residual solution was withdrawn about 3 mL during interval time of the adsorption process for 5, 15, 30, 45, 60, 90, 120, 150 and 180 min, respectively and then investigated the absorbance by using UV-visible spectrophotometer.

$$\text{Removal efficiency (\%)} = ((C_0 - C_t) / C_0) \times 100 \quad (1)$$

Where C_0 (mg/L) and C_t (mg/L) are the concentration of dye at initial (no adsorbent) and any (t) time (min).

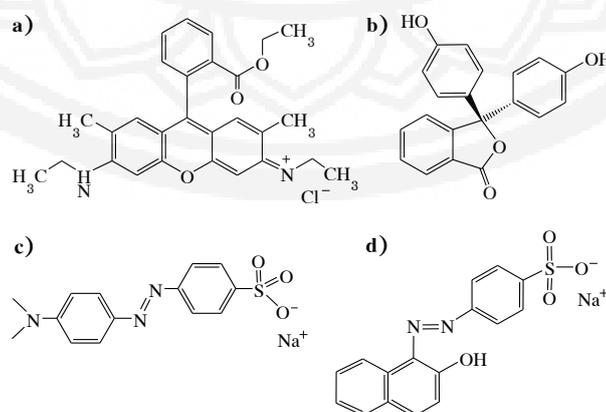


Figure 1 Chemical structure of rhodamine 6G (a), phenolphthalein (b), methyl orange (c) and orange II (d)



Results

Figure 2 shows the colored solid and morphology of NiAl-LDO and NiAl-LDH. After calcination, the change in the color was observed from green due to NiAl-LDH (Figure 2a) to dark gray due to NiAl-LDO (Figure 2b), attributing to the change in the coordination sphere due to Ni²⁺ based species in the LDO. It was thought that the dark gray might cause of NiO (dark gray) due to the oxidation of Ni²⁺(OH)₂ to be NiO based species (Lv et al., 2018). The SEM image of NiAl-LDH (Figure 2c) showed sheet or disc-like shape that resulted from numerous particles aggregated on the substrate according to the previous reports (Lv et al., 2018; Bai et al., 2019). Meanwhile, the sheet-like morphology of NiAl-LDO (Figure 2d) had been maintained after calcination that was just deintercalation of carbonate in the interlayer space with resulting in only delamination and then oxidation. The results might suggest the success in preparation of NiAl-LDO by calcination of NiAl-LDH. For further confirmation, the powder XRD patterns of NiAl-LDO and NiAl-LDH were investigated. The XRD pattern of NiAl-LDH revealed the (003) reflection and basal spacing (d_{003}) with 0.75 nm corresponding to the hydroxide-like structure of the LDH intercalated with carbonate, interpreting to the formation of NiAl-LDH (Lv et al., 2018). It can be seen the XRD peaks at about 37.72, 43.88 and 63.20° and the corresponding basal spacing (d) about 0.24 nm, 0.21 nm and 0.15 nm for the calcined product (Figure 3a) where the 2θ positions were indexed to (111), (200) and (220) diffraction owing to NiO, respectively (JCPDS 01-1239).

Besides, the functional groups of NiAl-LDO and NiAl-LDH were also studied by using FTIR spectra (Figure 4). The FTIR spectra of NiAl-LDH showed the characteristic bands at 3449, 1361, 992, 784 and 417 cm⁻¹, assigning to OH groups (stretching), carbonate (stretching and bending) and M–O (stretching and bending), respectively (Lv et al., 2018). Meanwhile, the absorption spectrum of NiAl-LDO (Figure 4a) showed the disappearance of the characteristic band due to carbonate at about 1361 cm⁻¹ after calcination treatment, and the appearance of the absorption bands at 3434 and 1629, as well as 779 and 471 cm⁻¹ due to OH group (water) and M–O (Ni–O and/or Al–O), respectively.

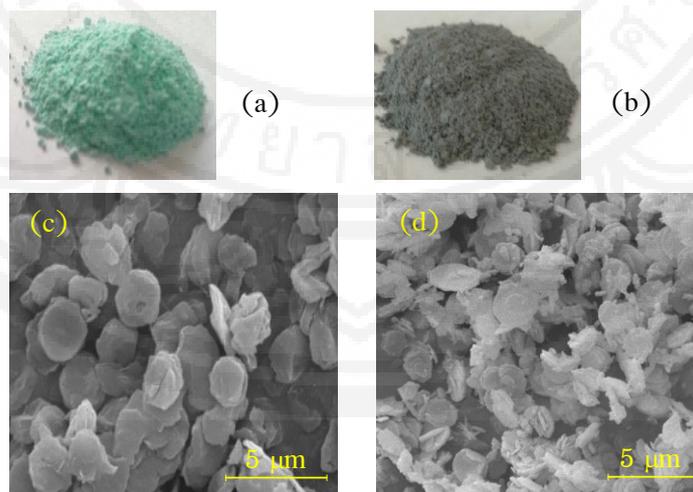


Figure 2 Color of NiAl-LDO (a) and NiAl-LDO (b), and SEM image of NiAl-LDO (c) and NiAl-LDO (d)

Table 1 Properties of the adsorbent with surface area, total pore volume and removal efficiency of orange II

Adsorbent	Surface area (m ² /g)	Total pore volume (cm ³ /g)	Removal efficiency (%)
NiAl-LDO	238.4	0.68	100
NiAl-LDH	85.2	0.46	70

To study the optical property of the product, the diffuse reflectance absorption spectrum of NiAl-LDO (Figure 5a) was conducted together with that of NiAl-LDH (Figure 5b). The absorption spectrum of NiAl-LDH showed the absorption bands at about 377 and 650 nm that resulted from the d-d transition due to Ni²⁺ ion (Wang et al., 2010). As the formation of major NiO based component in NiAl-LDO after calcination (from XRD result), the absorption bands of the calcined product were observed at 247 nm due to the charge transfer of oxo species (O₂, O²⁻) to metal (Ni²⁺), and at 413 and 735 nm due to the d-d transitions of Ni²⁺ in octahedral (or pseudo-octahedral symmetry) where are the ³A_{2g}(F) → ³T_{1g}(P) and ³A_{2g}(F) → ³T_{1g}(F) transitions, respectively (Emayavaramban, Ganesh Babu, Karvembu & Dharmaraj, 2010).

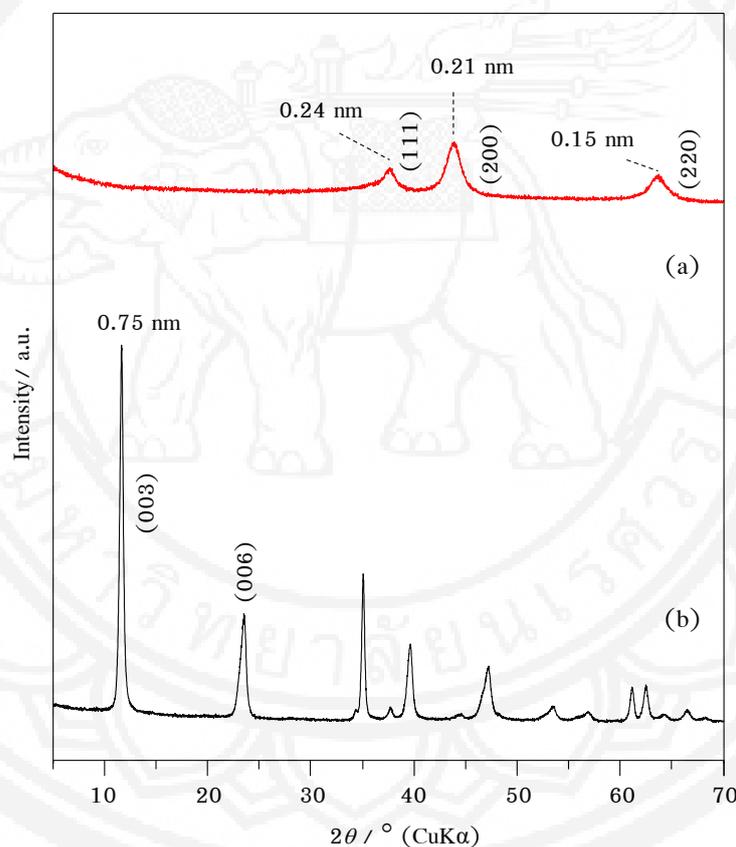


Figure 3 XRD patterns of NiAl-LDO (a) and NiAl-LDH (b)

Generally, the adsorption procedures occur on surface of adsorbent where the surface area is larger, the adsorption capacity is higher, thus the surface area and pore volume of NiAl-LDO and NiAl-LDH were comparatively investigated. The data are summarized in Table 1. By the surface modification of the LDH by calcination treatment, the specific surface area of NiAl-LDO was increased to 238.4 m²/g in comparison with NiAl-LDH (from 85.2 m²/g). Besides, the total pore volume of the NiAl-LDO (0.68 cm³/g) was larger



than that of the NiAl-LDH ($0.46 \text{ cm}^3/\text{g}$). The results were respect to the elimination of the intercalated water and carbonate during calcination process. It was possible that numerous sheets of NiAl-LDO were disorderly interlaced each other, leading to larger pore volume and resulting surface area.

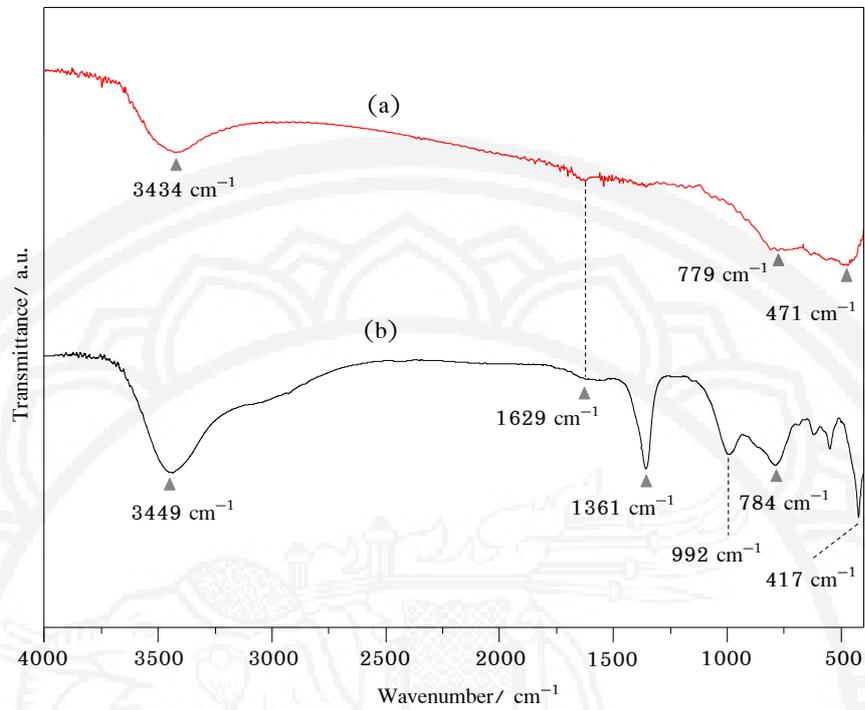


Figure 4 Fourier transform infrared (FTIR) spectra of NiAl-LDO (a) and NiAl-LDH (b)

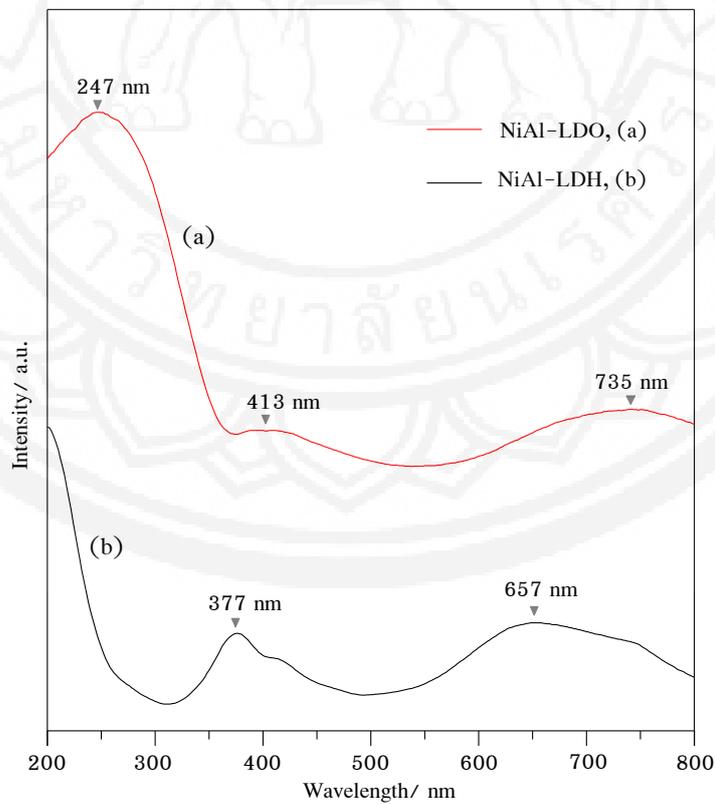


Figure 5 Diffuse reflectance absorption spectra of NiAl-LDO (a) and NiAl-LDH (b)

The adsorption of dye from solution rhodamine 6G, phenolphthalein and methyl orange (and orange II), was examined by using NiAl-LDO and NiAl-LDH as the adsorbent. These dye species are used as the representative of the toxic pollutants contaminated in water resource with cationic, neutral and anionic molecules, respectively (Figure 1). To examine the effect of geometric structure on the interaction between positively charged surface of the adsorbent and anionic dye molecule, methyl orange and orange II were comparatively evaluated. As a result of larger surface area, NiAl-LDO showed higher efficiency for eliminating dye molecules in a series of rhodamine 6G < phenolphthalein < methyl orange < orange II from solution than that of NiAl-LDH as shown in Figure 6 and the data are collected in Table 1. At various reaction time, the adsorption reaction occurred fast at the first contact time until the equilibrium at about 60 min, and then proceeded steadily. In addition, two dye (methyl orange and orange II) species with negative charge were mostly adsorbed on both adsorbents in comparison with those due to neutral and positive charge dye molecules, respectively. The result was consistent with the chemical adsorption respect to the electrostatic interaction due to chemical bonding of positive-charged surface of the adsorbent with anionic dye molecule, and/or the reconstruction of the LDH from NiAl-LDO was possible due to the memory effect (Gao et al., 2010; Lv et al., 2018; Bai et al., 2019).

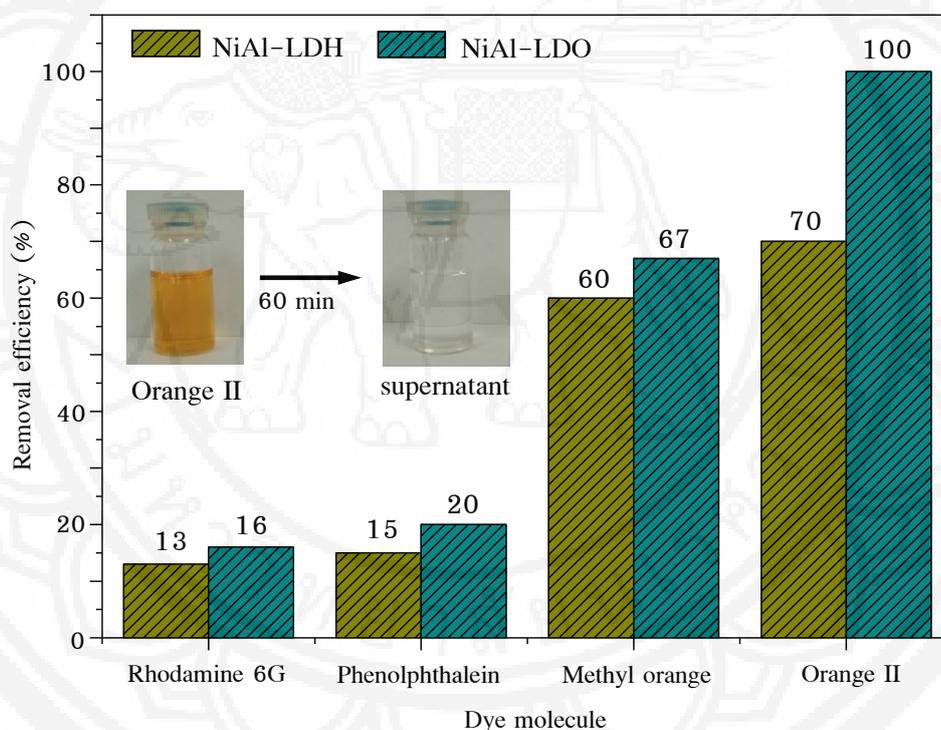


Figure 6 Removal efficiency of various dye molecules using NiAl-LDO and NiAl-LDH as the adsorbent

Discussion

The XRD result confirmed the presence of NiO in the calcined product (NiAl-LDO) derived from calcination of NiAl-LDH. After calcination, any XRD reflection due to Al_2O_3 was not seen on the XRD pattern of NiAl-LDO, this was because of the very low crystallinity and lower weight ratio compared to that of Ni^{2+} cation (Lv et al., 2018). From the FTIR result, it can be seen that almost absorption bands due to NiAl-LDH were observed, excluding of the absorption band due to the intercalated carbonate (at 1361 cm^{-1}), indicating to the



absence of layer structure connecting with the electrostatic attraction between anionic species and positive-charge layer. It can be seen the optical changes of NiAl-LDO in high absorption baseline (200–800 nm) and intense absorption resulting from mixed metal oxide that classified in semiconductor materials, thus the difference in various utilizations such as light absorber, catalyst, catalyst support and so on may be available. It can be seen (Figure 6) that orange II molecules were adsorbed more than that of methyl orange on NiAl-LDO adsorbent, it was thought that orange II could be adsorbed larger on the external surface and in the interlayer space (reconstruction of the LDH). This result was due to the rigid structure of orange II with diagonal shape compared to the flexible and linear shape of methyl orange, promoting anionic (oxygen, Figure 1) atom binding to the surface of the adsorbent in the vertical and/or tilt position. The modification of NiAl-LDH via calcination treatment showed the tailor of dye adsorption, in addition to, versatile for various dye species with different charge including of negative > neutral > positive.

Conclusions

NiAl-layered double oxide was successfully prepared by calcination treatment of NiAl-layered double hydroxide at 400 °C for 120 min corresponding to the confirmation from XRD and FTIR results, as well as UV-visible spectroscopic observation. The calcined product exhibited the larger surface and average pore volume when compared to those of the pristine layered double hydroxide. The adsorption capacity of the calcined product was higher than that of the uncalcined one as a result of the modification of the surface characteristic and host-guest interaction. NiAl-layered double oxide could be a smart adsorbent based on removal of orange II (100%), methyl orange (67%), phenolphthalein (20%) and rhodamine 6G (16%) where the tailor of the dye adsorption was as the factor on dye charge with negative, positive and neutral, respectively. Besides, the rigid structure with diagonal shape of anionic dye molecule was a significant factor on the adsorption efficiency.

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