

Efficient and practical adsorption of mixed anionic dyes in aqueous solution by magnetic NiFe-layered double oxide

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Abstract—The present research reports the adsorption capacity of magnetic NiFe-layered double oxide (NiFe-LDO) derived from the heat treatment of NiFe-layered double hydroxide (NiFe-LDH) on capturing of single anionic dye and mixed dyes in water. The formation and characteristics of NiFe-LDH and NiFe-LDO were verified by XRD, FT-IR, SEM, BET, VSM and UV-VIS. The obtained NiFe-LDO was mainly composed of NiFe₂O₄ and NiO phases, which showed strong magnetic property and made the adsorbents easily collected by external magnet. The amounts of the anionic dyes were captured on NiFe-LDO surface more than that on NiFe-LDH surface due to the larger surface area (68 m²/g for NiFe-LDO and 50 m²/g for NiFe-LDH). The maximum adsorption capacity of NiFe-LDO was in the range of 256-313 mg/g and 244-300 mg/g for eliminating the anionic dyes in single and multiple dye solution, respectively. The chemical adsorption affinity of the anionic dyes on the positive-charge surface of NiFe-LDO increased as follows: methyl orange < alizarin red S < orange II < Congo red. This work shows that NiFe-LDO is an efficient and cost-effective adsorbent for eliminating multiple anionic dyes and reusing for several times.

Keywords: NiFe-Layered Double Oxide, NiFe-Layered Double Hydroxide, Congo Red, Orange II, Alizarin Red S, Methyl Orange

INTRODUCTION

Water is indispensable to human, plant and animal life, especially clean water [1]; therefore, the contamination from chemicals and other toxic species in natural water resource is a major problem that must be urgently solved [2]. Synthetic dye is a principal of fatal pollutants because of several serious intoxications and much of the rest of dye after dyeing processes [3,4]. Due to a variety of structural charges (anion, cation and neutral) and high stability, numerous dyes have accumulated within biosystems for long period of time. The unique and potential methods such as photocatalysis, adsorption, physical and biological treatments have been studied to remove the dangerous dyes in water [5,6]. Among all the processes, adsorption shows a few superior advantages; for example, practical and efficient procedure for quick removal of the large amount of dyes in wastewater, but an efficient and practical adsorbent is necessary [3,4]. Inorganic adsorbents, including zeolite, metal organic frameworks, activated carbon, and graphene oxide, are intensively synthesized to optimize the adsorption performance [7-11]. Among those adsorbents, layered inorganic solids and their composites have received more interest because of their great adsorption capacities that can selectively eliminate versatile toxic chemicals, including hazardous anion and cation, polymer, drug, insecticide and pesticides

in water [12,13]. Because the diversity of the adsorbent structures is necessary for the optimization of the dye removal efficiency with different and/or extraordinary properties, the use of a positive or negative-charge surface adsorbent may lead to the great adsorption ability of charged and neutral dyes via electrostatic and physical interactions.

Layered double hydroxide (LDH), a typical formula of $[M^{2+}M^{3+}(\text{OH})_2]^{m+}(A^{n-})_{m/n} \cdot x\text{H}_2\text{O}$, has a variety of structures that can be fabricated by varying different divalent (M^{2+}) and trivalent (M^{3+}) metal ions used as central atoms, and counter anions (A^{n-}) in the inter-layer space. Due to the nice combination in the layered structure, LDH provides a large surface area, swelling behavior, stability, optical and/or magnetic properties and so on [14-16]. Meanwhile, layered double oxide (LDO) is availably carried out by calcination treatment of LDH to decompose the interlayer anion and carry out the *in situ* oxidation of hydroxide-sheets [17-22]. Interestingly, LDO shows superior properties to its precursor, such as large surface area, and high stability in acid-base solution, light irradiation and heat treatment [23,24]. As a result, LDO can be used as a catalyst, catalyst support, adsorbent, light absorber and so on [14,16,25]. Therefore, the usage of LDH and LDO for the elimination of mixed anionic dyes in water is worth investigation.

In this study, NiFe-LDH and NiFe-LDO were prepared and used as the adsorbent for the elimination of anionic dyes. The toxic dyes contaminating wastewater have been mostly cleaned by adsorbing onto LDO and/or LDH surfaces [17,19,26]. It was reported that the usage of magnetic NiFe-LDH composite as the adsorbent has pro-

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moted an easier way to magnetically separate the composite from solution [27]. NiFe-LDH and/or NiFe-LDO have been used as a potential adsorbent for removing of single dye [19,23,24,28,29], but their magnetic separation property and capacity on removing of anionic dye mixtures and/or reusability have not been reported so far. Herein, the first comparative study on removing single and mixed anionic dyes (methyl orange, alizarin red S, orange II and Congo red) in aqueous solution by using NiFe-LDH and NiFe-LDO adsorbents, and their magnetic property is also reported, which may be a valuable and simple pathway for wastewater purification.

EXPERIMENT

1. Materials

Nickel(II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) used as divalent and trivalent metal ions, respectively, were obtained by Carlo Erba Reagenti. Trisodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) was purchased from Unnma. Urea ($(\text{NH}_2)_2\text{CO}$) was supplied by Asia Pacific Specialty Chemicals LTD. Methyl orange ($\text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S}$), alizarin red S ($\text{C}_{14}\text{H}_7\text{NaO}_7\text{S}$), orange II ($\text{C}_{16}\text{H}_{11}\text{N}_2\text{NaO}_4\text{S}$) and Congo red ($\text{C}_{32}\text{H}_{22}\text{N}_6\text{Na}_2\text{O}_6\text{S}_2$) were made by Acros. All chemicals are the reagent grade and were used directly without any further purification.

2. Preparation of the Magnetic Adsorbents

NiFe-LDH was carried out by hydrothermal reaction through urea hydrolysis. 1.2 mmol $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.4 mmol $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in deionized water and mixed under magnetic stirring. Then an aqueous solution of 2.8 mmol $(\text{NH}_2)_2\text{CO}$ and an aqueous solution of 0.02 mmol $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ were added in the resulting solution under continual magnetic stirring for 10 min. The molar ratio of $\text{Ni(II)} : \text{Fe(III)} : (\text{NH}_2)_2\text{CO} : \text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ was 3 : 1 : 7 : 0.2 in totally 80 mL of deionized water. The transparent yellowish green solution was hydrothermally reacted at 150 °C for 48 h. The obtained NiFe-LDH was collected by centrifugation, washed several times with deionized water, and then ethanol, finally heated at 60 °C. For the preparation of NiFe-LDO, an appropriate amount of NiFe-LDH was placed in a crucible and calcined at 400 °C for 2 h.

3. Removal of Dye Ions in Aqueous Solution

The adsorption capacity of the adsorbents was evaluated by transferring the dyes (methyl orange, alizarin red S, orange II and Congo red) from the solution to their surfaces. Briefly, 20 mg of adsorbent (NiFe-LDH or NiFe-LDO) was magnetically dispersed in 30.0 mL of 30 ppm dye solution for 5, 10, 20, 30, 40, 50 and 60 min in the dark region (at about 27 °C). The adsorbent powder was collected using the external magnet and the remaining dye solution was taken to measure the absorbance by using UV-visible spectrophotometer. For competitive study, the mixed dyes solution (methyl orange, alizarin red S, orange II and Congo red) in total volume of 120 mL was prepared by using 30 mL of 30 ppm of each dye solution, and various amount of the adsorbents (90, 120, 150, 180, 210, 240, 270 and 300 mg) was added in the solution and mixed well. To obtain the thermodynamic parameters, the adsorption reaction of the mixed dyes system was carried out at temperature of 303, 323 and 343 K using 210 mg of the adsorbents.

To investigate the absorbance of each dye in aqueous solution,

the maximum absorption wavelength of methyl orange, alizarin red S, orange II and Congo red was fitted at 462, 512, 486 and 498 nm, respectively. Whereas, each dye in the mixture solution showed its characteristic absorption band that corresponded to its initial diluted concentration and further proved by non-linear Lorentz model. After use, the dyes-adsorbent was cleaned by the calcination treatment at 400 °C for 2 h before being reused for the next batch till the fourth cycling test. The adsorption isotherm, kinetic and thermodynamic, and the corresponding parameters were determined by fitting of the adsorption data using the equations as shown in Table S1.

4. Characterization

Powder X-ray diffraction (XRD) patterns were carried out on a Bruker D8 ADVANCE diffractometer using monochromatic $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Fourier transform infrared (FT-IR) spectra of the solid samples were recorded on a Perkin Elmer Spectrum One FT-IR spectrophotometer by KBr disk method. Scanning electron microscope (SEM) images were conducted on an FEI Helios Nanolab G3 CX DualBeam FIB-SEM operated at 10 kV. Nitrogen adsorption/desorption isotherms were obtained on a Micromeritics ASAP 2010 equipment, after the sample was degassed at 120 °C under vacuum for 3 h. Magnetic characteristic was measured on a Lake Shore - 7403 series vibrating sample magnetometer (VSM) with applied magnetic field of ± 1.50 Tesla (T). Diffuse reflectance absorption spectra of the powder samples were conducted on a Shimadzu UV-VIS-NIR 3101PC spectrophotometer in the range of 200–800 nm using an integrated sphere. UV-visible absorption spectra of the dye solution were measured on a Shimadzu UV-1700 Pharmaspec UV-VIS spectrophotometer. The zeta potential was conducted at 25 °C on a Zetasizer (Nano ZS, Malvern, Worcestershire, UK) by using water as a dispersant. Thermogravimetric-differential thermal analysis (TG-DTA) curves were performed in the temperature range of 50–950 °C on a Perkin Elmer Pyris Diamond TG-DTA instrument under a dry-air flow at heating rate of 10 °C min^{-1} using α -alumina ($\alpha\text{-Al}_2\text{O}_3$) as the standard material.

RESULTS AND DISCUSSION

1. Characterization

The structural phase of both NiFe-LDH and NiFe-LDO was verified by the XRD patterns. The diffraction peaks appearing at $2\theta = 11.39^\circ$ and 22.96° (Fig. 1(a)) were ascribed to the (003) and (006) reflections of NiFe-LDH, respectively (JCPDS no. 40-0215) [24], confirming the formation of NiFe-LDH. The (311) reflection observed at $2\theta = 35.78^\circ$ was due to the spinel NiFe_2O_4 phase that grew together with NiFe-LDH during the hydrothermal reaction and might promote the magnetization [30]. The basal spacing of the (003) diffraction was of 7.77 Å that matched to the size of carbonate (CO_3^{2-}), indicating the intercalation of carbonate ions in the interlayer nanospace [23].

After the calcination, the (003) diffraction was dismissed in the XRD pattern of NiFe-LDO (Fig. 1(b)) due to the decomposition of the carbonate in the interlayer space. The result could be ascribed to the delamination of the LDH structure and the *in situ* construction of the LDO sheets [30,31]. Meanwhile, the formation of NiFe_2O_4 and NiO was clearly observed by the appearance of the diffraction

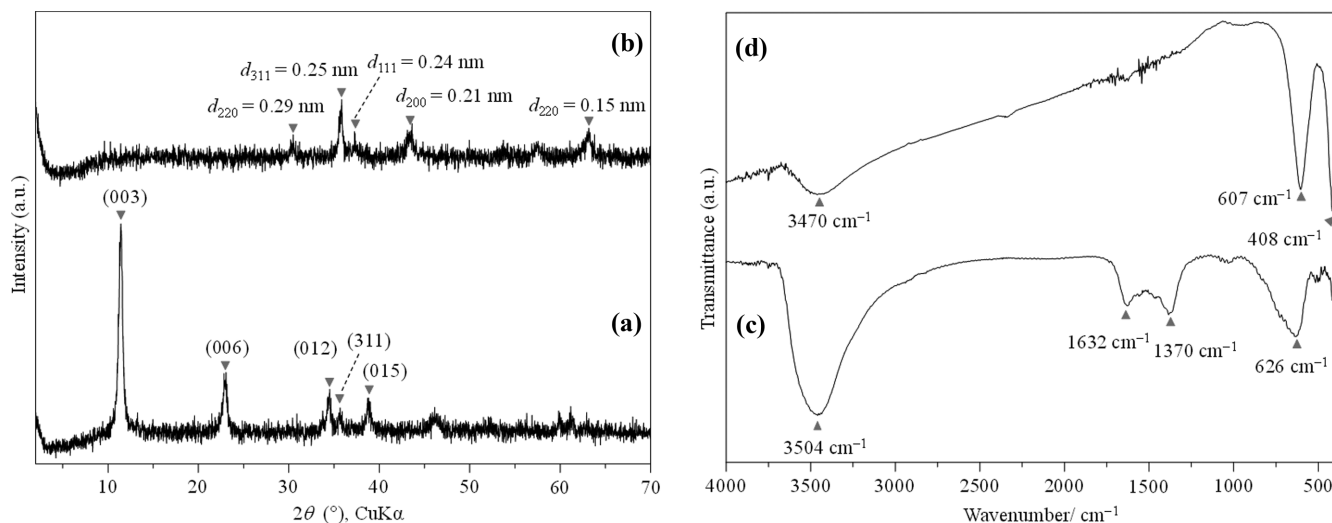


Fig. 1. XRD patterns of (a) NiFe-LDH and (b) NiFe-LDO, and FT-IR spectra of (c) NiFe-LDH and (d) NiFe-LDO.

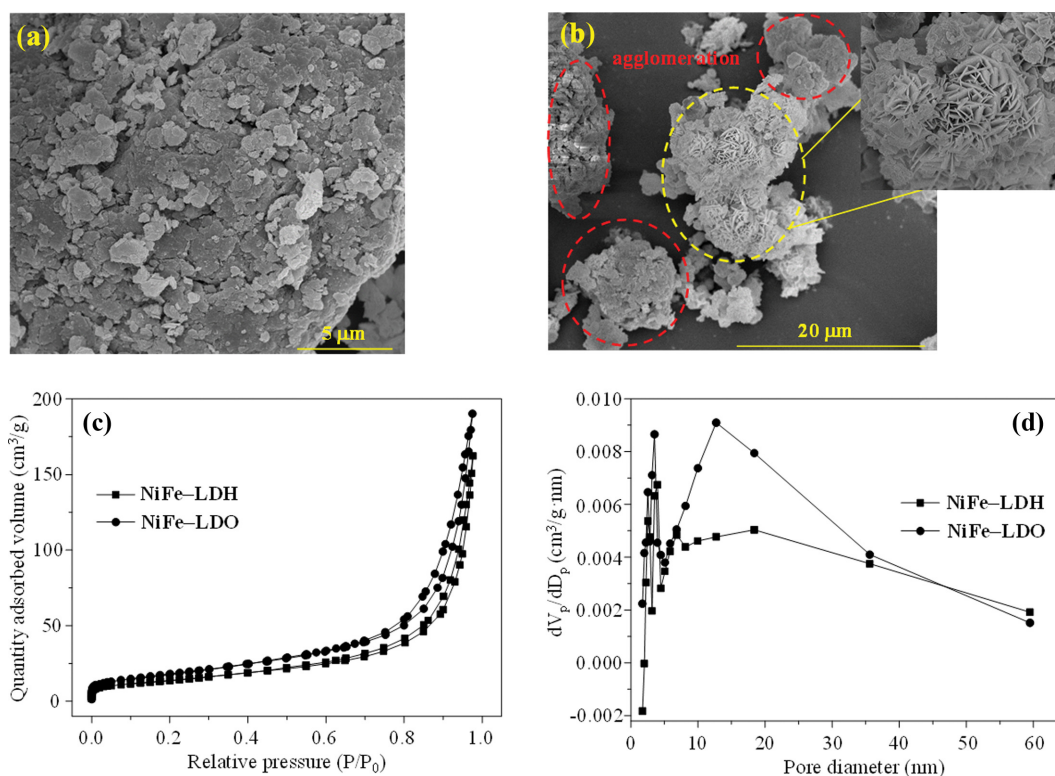


Fig. 2. SEM micrographs of (a) NiFe-LDH and (b) NiFe-LDO, and (c) N_2 adsorption-desorption isotherms and (d) pore size distribution of NiFe-LDO and NiFe-LDH.

peaks at $2\theta=30.45^\circ$ (220) and 35.78° (311) due to the spinel phase of $NiFe_2O_4$, JCPDS no. 54-0964 [30], and at $2\theta=37.33^\circ$ (111), 43.37° (200) and 63.07° (220) due to NiO, JCPDS no. 47-1049 [23], supporting the formation of mixed divalent and trivalent metal oxides in NiFe-LDO [29,31].

The infrared spectrum of NiFe-LDH (Fig. 1(c)) showed absorption bands at 3504 , 1370 and 626 cm^{-1} , which were attributed to the O-H and CO_3^{2-} as well as M-O stretching vibration modes of the interlayer water molecules and carbonate, as well as metal-oxide,

respectively [31]. Meanwhile, the FT-IR band at 1370 cm^{-1} was not observed for NiFe-LDO (Fig. 1(d)) due to the absence of the carbonate ions in the interlayer space. Additionally, the FT-IR bands at 408 and 607 cm^{-1} were assigned to the M-O and/or M-O-M stretching vibration modes of NiO and/or $NiFe_2O_4$ [23], corresponding to the XRD result, supporting the delamination of NiFe-LDH and the formation of NiFe-LDO sheets.

The morphology of NiFe-LDH and the change in its morphology after the calcination (NiFe-LDO) were displayed on SEM images.

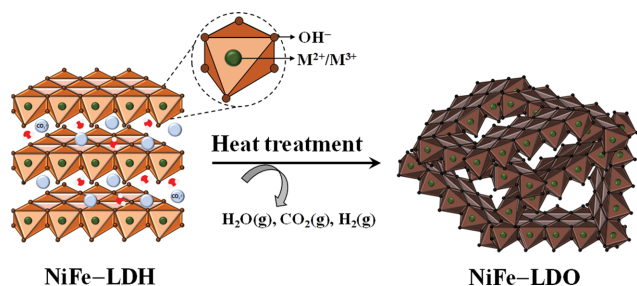


Fig. 3. Proposed structures of NiFe-LDO and NiFe-LDH.

Clearly seen is that NiFe-LDH (Fig. 2(a)) possessed a sheet-like structure in terms of the aggregation of several hexagonal-shaped particles [15,18,24,31]. The dense packing of the NiFe-LDH sheets was due to the presence of the interlayer carbonate, corresponding to a layer-by-layer structure. Meanwhile, a sheet-like morphology was also observed on the SEM image of NiFe-LDO with the disordered arrangement (Fig. 2(b)) due to the loss of the bridging carbonate anions that formed the lamellar architecture [20,21]. Evidently, the disorderly layered structure of the LDO was formed, where several NiFe-LDO sheets with the thickness about 50–100 nm were placed randomly due to the repulsive interaction among the positively charged surface [20,22].

The size, pore volume, as well as the specific surface area of the adsorbents were examined by surface analysis. The N_2 adsorption-desorption isotherms of NiFe-LDH and NiFe-LDO were classified as type IV with H3 hysteresis loop (Fig. 2(c)), which is indicative of a mesoporous material [20]. The size distribution of pore volume (Fig. 2(d)) was in the range of 8–27 nm, where the pore volume of NiFe-LDO ($0.29 \text{ cm}^3/\text{g}$) was larger than that of NiFe-LDH ($0.25 \text{ cm}^3/\text{g}$), supporting the delamination of the layered structure and the absence of the interlayer carbonate. The arrangement of the LDO sheets with the wedge-like pore is proposed in Fig. 3 [18]. The presence of the intercalated species in the interlayer space of NiFe-LDH made the pore volume lower, and expanded the aver-

age pore size of NiFe-LDH ($\sim 20 \text{ nm}$) larger than that of NiFe-LDO ($\sim 17 \text{ nm}$). Besides, the elimination of the interlayer carbonate anions and water molecules promoted the larger specific surface area for NiFe-LDO ($68 \text{ m}^2/\text{g}$) in comparison with NiFe-LDH ($50 \text{ m}^2/\text{g}$). Considering the BET surface area in Table 1, the NiFe-LDH and NiFe-LDO possessed a larger surface area than those of the other adsorbents reported previously. The variation in surface area might be caused by the preparation procedure, reacting time and temperature, as well as the re-arrangement of structure.

2. Magnetic and Optical Properties

The hysteresis loops of both products were according to the superparamagnetism that corresponded to very low values of coercivity and retentivity (about=0) with the high saturation magnetization of 5.01 emu/g for NiFe-LDH and 28.01 emu/g for NiFe-LDO [32]. Besides, their saturation magnetizations were greater than those of $\text{CoFe}_2\text{O}_4/\text{CuAl-LDH}$ and APT/C@NiFe-LDH (Table 1). After the heat treatment, NiFe-LDO showed an increase of the saturation magnetization of about six times due to the increase of spinel NiFe_2O_4 phase [30]. The strong magnetic interaction of NiFe-LDO or NiFe-LDH with the external magnet is displayed in Figs. 4(a) and 4(b). The big gap of the saturation magnetization (23 emu/g) significantly improved the magnetic property of NiFe-LDO and made it easy and efficient to be rapidly collected from the solution (within 1 min) by using the external magnet.

The absorption characteristic of NiFe-LDH (Fig. 4(c)) and NiFe-LDO (Fig. 4(d)) was investigated. The UV energy region observed in the wavelength range of 240–260 nm and 320–350 nm was generated by the ligand to metal charge transfers from the O_{2p} to Ni_{3d} and Fe_{3d} , respectively. Clearly seen in the spectrum of NiFe-LDH (Fig. 4(c)), the d-d transitions of Ni^{2+} ions in the octahedral crystal field at 380 and 750 nm were due to ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$, respectively. In addition, the small shoulders at around 380–750 nm were attributed to the spin-forbidden transitions of ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^1\text{T}_{2g}(\text{D})$ and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^1\text{E}_g(\text{D})$ [33,34]. Meanwhile, the broad spectrum of NiFe-LDO observed at 370–700 nm arose from the differences in the surrounding environment of center atom, crystallinity,

Table 1. Surface properties and magnetization of the products, and the comparative characteristics to other adsorbents

Sample	Preparation method of LDH or LDO	BET surface area (m^2/g)	Saturation magnetization (emu/g)	Reference
NiFe-LDH	Hydrothermal at 150°C , 48 h	50	5	This work
NiFe-LDO	Calcination at 400°C , 2 h	68	28	This work
Calcined CoAl-LDH	Calcination at 350°C , 3 h (N_2)	41.4	-	[24]
Calcined NiFe-LDH		17.1	-	
$\text{CoFe}_2\text{O}_4/\text{CuAl-LDH}$	co-Precipitation	89.0	0.025	[42]
$\text{CoFe}_2\text{O}_4/\text{CuAl-LDO}$	Calcination at 500°C , 4 h	17.6	~ 0.05	
LDH8	co-Precipitation ($\text{pH}=8$), Hydrothermal at 150°C , 24 h	41	0.96	[34]
NiFe-LDH	Hydrothermal at 180°C , 24 h	60	-	[23]
NiFe-LDH	Calcination at 400°C , 4 h	121	-	
ZnAl-LDH	Reaction by urea hydrolysis at 100°C , 8 h	16.6	-	[20]
ZnAl-LDO	Calcination at 600°C , 6 h	55.9	-	
NiFe-LDH	co-Precipitation	17.85	-	[28]
APT/C@NiFe-LDH	Hydrothermal at 180°C , 12 h	65.7	2.01	[27]

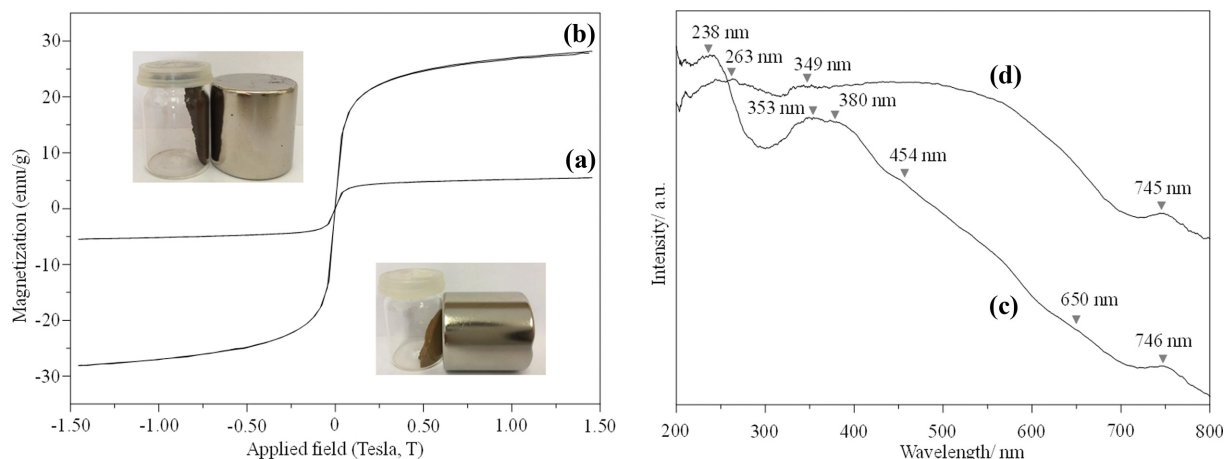


Fig. 4. VSM magnetization curves and the magnetic interaction of (a) NiFe-LDH and (b) NiFe-LDO, and UV-VIS spectra of (c) NiFe-LDH and (d) NiFe-LDO.

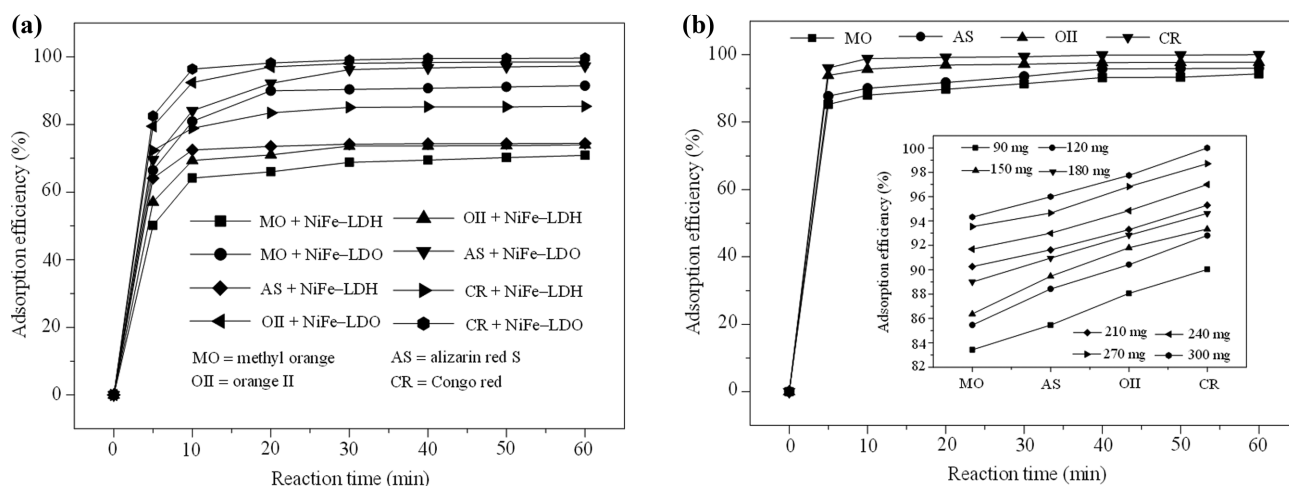


Fig. 5. Adsorption efficiency of (a) single dye and (b) mixed dyes by NiFe-LDO adsorbent.

defect including oxygen vacancy, and the interfacial interaction [33].

3. Adsorption Studies

The adsorption capacity was evaluated by removing the anionic dyes (methyl orange, alizarin red S, orange II or Congo red) and the mixed dyes in water. In the first 30 min of the contact time (Fig. 5(a)), the amounts of single dye ions were mostly captured onto the LDO surface with the removal efficiency of 90–99%, while the efficiency of the LDH was only 69–85%. Almost all of the dyes (methyl orange (86–94%), alizarin red S (89–96%) and orange II (93–98%)) in the mixed dyes solution could be removed by NiFe-LDH and NiFe-LDO (300 mg). For the mixed dyes system (Fig. 5(b), inset), the amount of each dye was additionally adsorbed onto the adsorbent surface with increasing the adsorbent dosage (90–300 mg). The adsorption of the dyes onto both NiFe-LDH and NiFe-LDO was increased in a series of methyl orange < alizarin red S < orange II < Congo red. As a result, the higher absorption capacity observed for NiFe-LDO for both single and mixed dyes systems was due to the larger surface area and the electrostatic interaction [28]. Congo red was the fastest removed dye from the solution; meanwhile, methyl orange (Fig. 6(a)) was the slowest removed

one for all systems (Fig. 5(b) and Fig. S1). It was thought that two negative sites and H-bonding sites of Congo red (Fig. 6(d)) played a key role in interacting with the positive-charge surface of NiFe-LDO. The difference in the adsorption percentage of methyl orange and Congo red onto the adsorbents might be due to the difference in the adsorption mechanism and the surface chemistry [15,35–37].

The pH optimization of Congo red in the aqueous solution was studied from 1–14 (Fig. S2); the highest adsorption efficiency was observed at the pH value of 5.0 for both NiFe-LDH and NiFe-LDO adsorbents. In acidic solution, the decrease in the adsorption capacity of NiFe-LDH (Fig. S2(a)) was due to the dehydration and destruction of the LDH [38]. Meanwhile, the adsorption ability of NiFe-LDO dropped by 20% from pH 5–1, indicating higher stability in the acidic solution. The available positive charge on the surface of NiFe-LDH and NiFe-LDO was represented by the zeta potential at the pH values of 8.20 and 8.43, respectively, while the zeta potential of Congo red showed a negative charge over all of the pH values (Fig. S3). The adsorption mechanism of Congo red on the adsorbent surfaces was assumed as the electrostatic interaction over the pH range of 2.0–8.2 for NiFe-LDH and 1.0–8.4 for

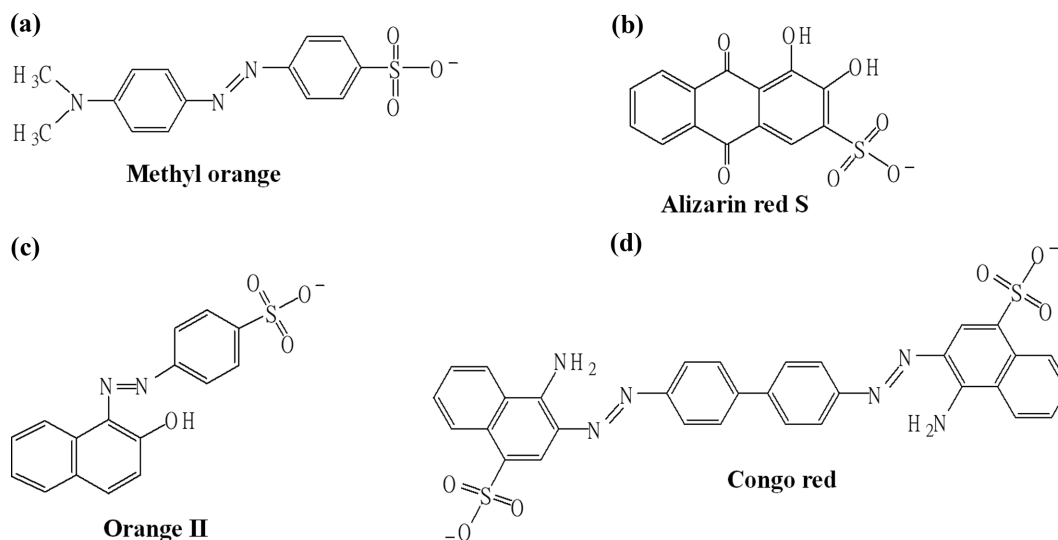


Fig. 6. Structure of (a) methyl orange, (b) alizarin red S, (c) orange II and (d) Congo red.

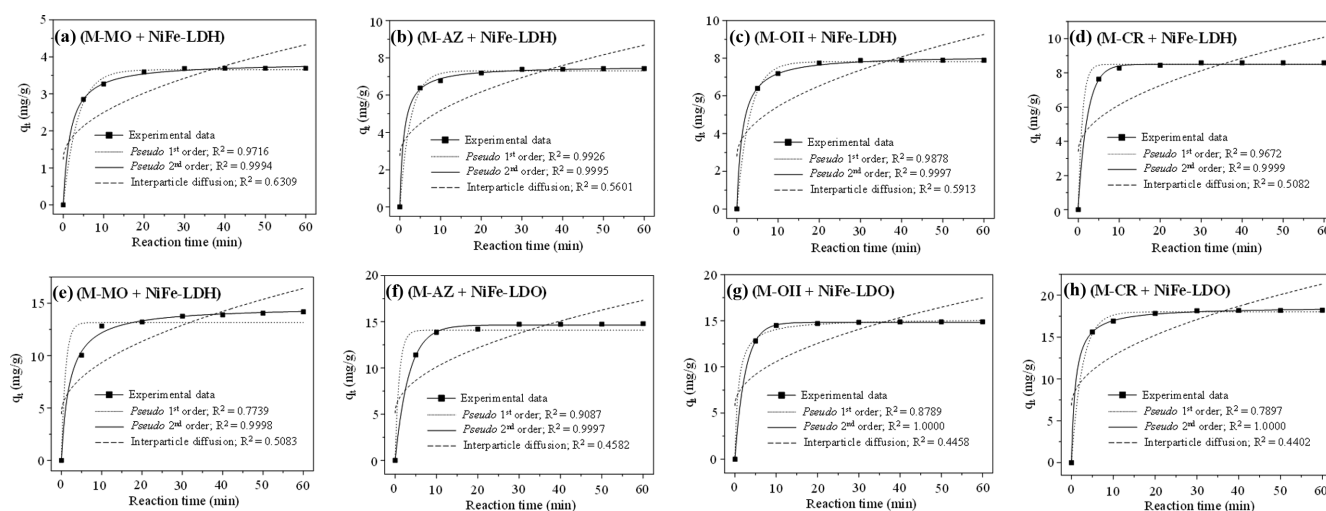


Fig. 7. Adsorption kinetics of mixed dyes fitted by non-linear pseudo-first-order, pseudo-second-order and intraparticle diffusion models of (a)-(d) NiFe-LDH and (e)-(h) NiFe-LDO.

NiFe-LDO. However, the correlation between the adsorption activity and the positive-charge surface of the adsorbents was not significantly affected by changing of the pH values. Therefore, to preserve cost and environment, these dye adsorption processes should be investigated without the pH adjustment (pH~5.2-6.1), as shown in Fig. 5 and Fig. S1.

The adsorption kinetic of the adsorbents was analyzed with the nonlinear chemisorption models (Figs. 7 and S4), where the equations are listed in Table S1. All adsorption reactions were agreeable to pseudo-second-order model ($R^2 \sim 1$) (Table S2), indicating that the adsorption of dyes onto the adsorbents was dependent on the dye concentration and the amount of the adsorbent. The higher adsorption capacity (q_m) and rate constant (K_2) (Table S2) of NiFe-LDO were thought to be due to the increase of specific surface area from 50 m²/g (NiFe-LDH) to 68 m²/g (NiFe-LDO). The adsorption data at various concentrations of all dyes were well fitted with the Langmuir isotherm and yielded the best fit for the kinetic

data with a regression constant, $R^2 > 0.99$ (Figs. 8 and S5), attributed to the favorable adsorption of the dyes onto the adsorbents. All the dyes (methyl orange, alizarin red S, orange II and Congo red) were adsorbed onto the surface of NiFe-LDH and NiFe-LDO as a monolayer with the capacity of around 165-300 mg/g (Table S3).

By comparison of the adsorption data fitted by both non-linear (Table S2) and linear (Table S3 and Fig. S6) equations using Langmuir and Freundlich analyses, the adsorption capacities (q_m) for non-linear and linear models were not significantly different. Thus, the maximum adsorption capacity was presented by using the Langmuir isotherm for the linear case ($q_m = 312.5$ and 300.1 mg/g for Congo red adsorbed onto NiFe-LDO in single and mixed dye solution, respectively). The dye-removal capacity of NiFe-LDO was increased (Table S3) as follows: methyl orange (243.9 mg/g) < alizarin red S (264.2 mg/g) < orange II (282.0 mg/g) < Congo red (300.1 mg/g), whereas that of NiFe-LDH was significantly lower, as a result of the lower active site and smaller surface area. The NiFe-LDH and

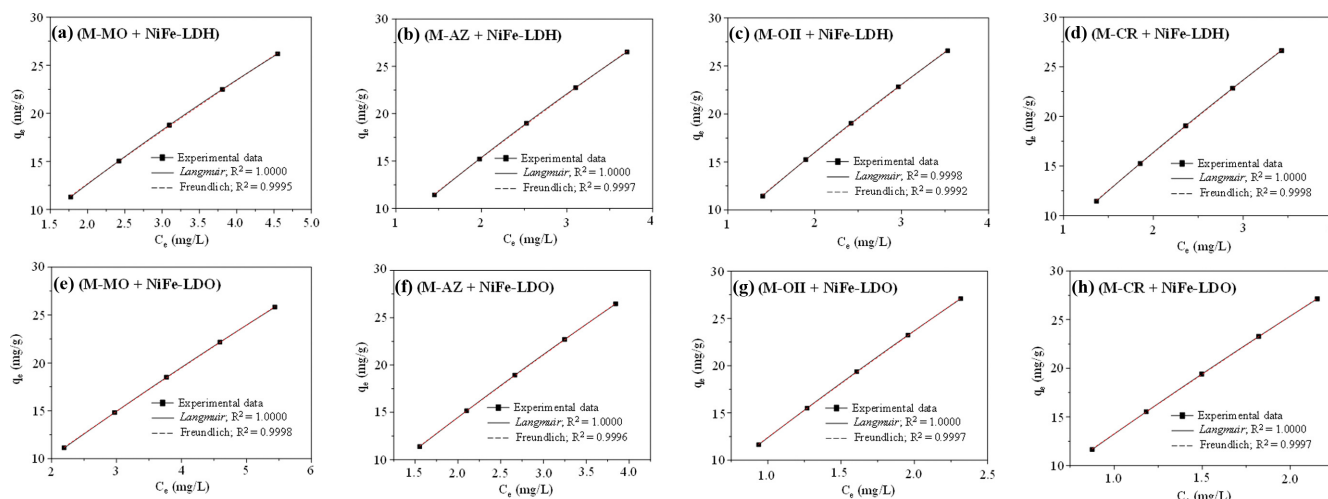


Fig. 8. Adsorption isotherms of mixed dyes fitted by non-linear Langmuir and Freundlich models of (a)-(d) NiFe-LDH and (e)-(h) NiFe-LDO.

Table 2. Maximum adsorption capacity (q_m) of various adsorbents on removing anionic dyes

Adsorbent	q_m (mg/g)				Reference
	MO	AR	OII	CR	
NiFe-LDH	166	181	195	218	This work
NiFe-LDO	244	264	282	300	This work
NiFe-LDH	-	-	-	205	[23]
NiFe-LDO	-	-	-	330	[23]
MOF@CA	-	-	-	280	[11]
LDH8	-	-	-	97	[34]
EW@ZIF-8@PAA aerogel	281	-	-	-	[10]
CoFe ₂ O ₄ -FGS	72	-	-	-	[7]
Mg-Al mixed metal oxide	182	-	-	-	[17]
NiFeTi LDH	33	-	-	30	[15]
NiFe-LDH	206	-	-	-	[28]
MMT@Ni ₄ Fe ₁ LDH	109	-	-	-	[29]
organo-palygorskite	-	-	96	-	[43]
ZnAl-LDH-W	-	-	42	-	[44]
CTAB-cornstalk biochar	-	-	27	-	[45]
ZnCr-LDH	-	-	204	-	[46]
Au-NP-AC	-	123	-	-	[47]
PEI@MCNTs	-	196	-	-	[48]
Fe-clay	-	33	-	-	[49]

MO=methyl orange, AR=Arizalin red S, OII=orange II, CR=Congo red

NiFe-LDO were expressed as the efficient adsorbents on eliminating methyl orange, alizarin red S, orange II and Congo red, when compared with the other adsorbent by the q_m value listed in Table 2.

The thermodynamic parameters of the dye adsorption in the mixture solution are listed in Tables S4 and S5. The adsorption of the mixed anionic dyes in aqueous solution onto the LDH and LDO surfaces showed the positive values of enthalpy change ($+\Delta H^\circ$), attributed to the endothermic reaction. The entropy change (ΔS°) of all systems was accompanied with high randomness ($+\Delta S^\circ$) at

the liquid-solid interface due to the movement of the dye ions through hydration shell onto the adsorbent surface under the electrostatic attraction [19,24,34,39]. Moreover, the negative values of Gibbs free energy change ($-\Delta G^\circ$) obtained at the different temperatures of 303, 323 and 343 K were more negative with increasing the temperature, which is indicative of a spontaneous reaction. As a result, the dyes were favorably adsorbed onto NiFe-LDH and NiFe-LDO surfaces with increasing the temperature. The proposed mechanism mainly involved hydrogen bonding, as well as ionic interactions, resulting in the strong capture between the dyes and the adsorbent.

4. Reusability

The adsorption performance of NiFe-LDO was tested on the recycling runs for mixed dyes removal (Fig. 9(a)). The adsorbent showed nearly steady efficiency on the removal of methyl orange, alizarin red S, orange II and Congo red from the dye mixture. After the fourth recycling time, the XRD pattern of NiFe-LDO (Fig. 9(b)) revealed the slight decrease in the reflection intensity, indicating the high stability of the adsorbent. No diffraction peak of the dye and/or another compound was observed, indicating that the adsorbed dye was completely removed from the surface of NiFe-LDO. Meanwhile, the SEM image (Fig. 10(a)), electron mapping (Fig. 10(b)), EDX spectrum (Fig. 10(c)), and UV-visible spectrum (Fig. 10(d)) also confirmed the remaining NiFe-LDO with the absence of the dye. In the TG curves (Figs. 10(e) and 10(f)), the mass loss observed in the temperature range of 50–200 °C was due to the evaporation of the adsorbed and coordinated water molecules. At the higher temperature range (200–950 °C), the mass loss of both samples was less than 2.5%, which might indicate the dehydroxylation and/or the decomposition of other contaminants [19], which corresponded to the broad exothermic characteristic peak in the DTA curves (Figs. 10(g) and 10(h)). The results indicated that NiFe-LDO was durable at high temperature, where the used NiFe-LDO adsorbent was simply cleaned by the thermal decomposition of the adsorbed dye; this is a cost-saving method compared to a leaching approach by alcohol, alkaline and/or acid solution [26]. In addition, this method is a useful way to self-regenerate NiFe-LDO after the adsorption.

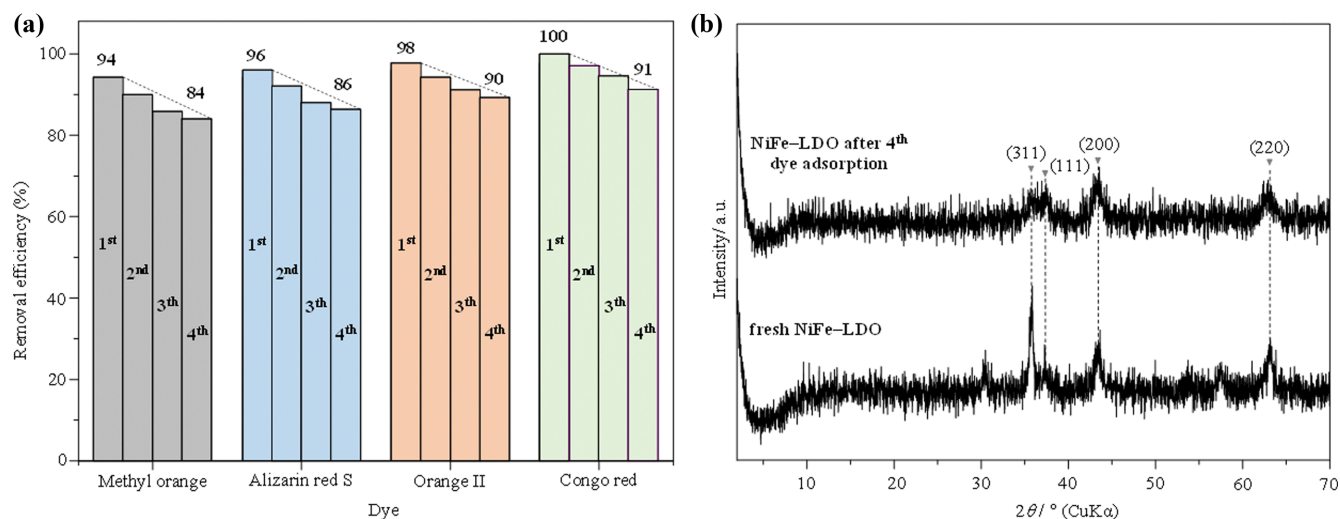


Fig. 9. (a) Recycle runs, and (b) XRD patterns of NiFe-LDO before and after the fourth dye adsorption.

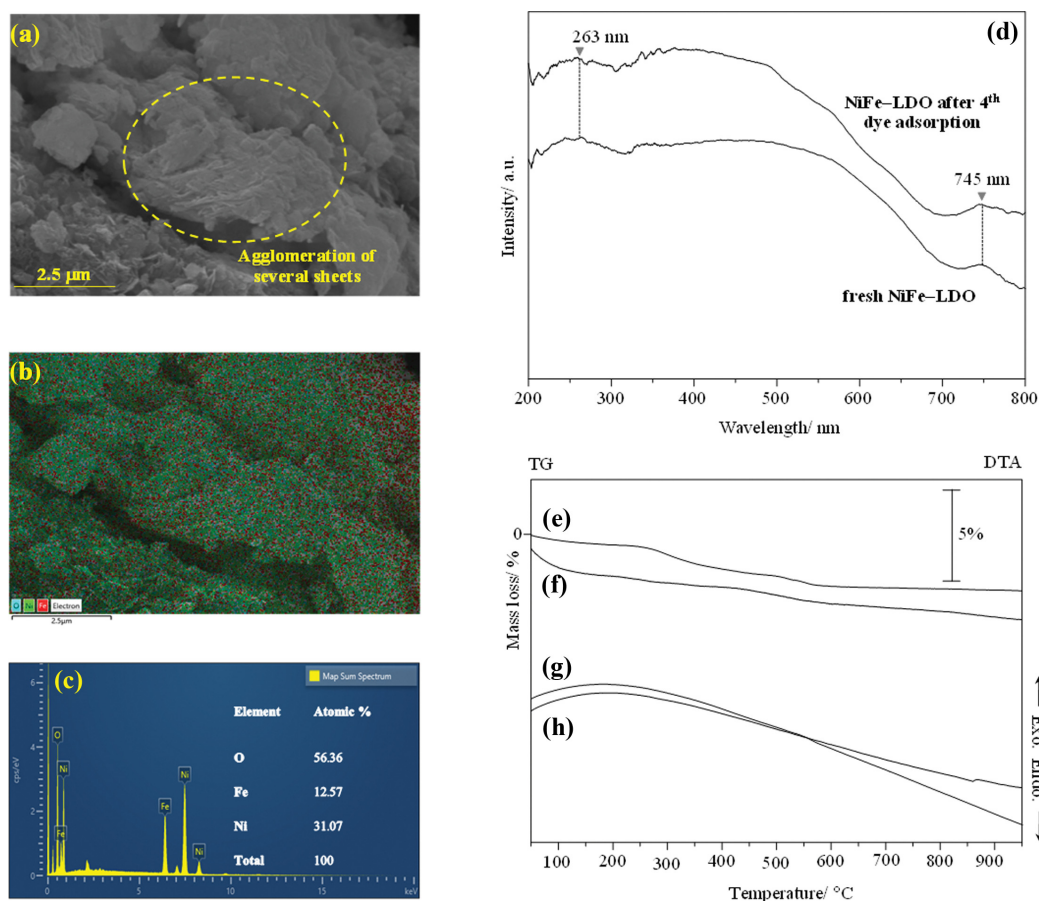


Fig. 10. (a) SEM image, (b) elemental mapping and (c) EDX spectrum of the used NiFe-LDO, and (d) UV-visible spectra and TG-DTA curves of NiFe-LDO ((e) and (g))before the dye adsorption and ((f) and (h)) after the fourth cycle use.

5. Cost Estimation

In the preparation of 20.0 g NiFe-LDH (10 g was used to prepare NiFe-LDO), the chemicals cost was very low (\$10), while the hydrothermal reactor (\$333) and electrical furnace (\$1,650) were one-time investments that cost only \$1/time and \$2/h, respectively.

All reactions or processes were carried out by using DI water (about 10 L) as solvent, which estimated the processing cost to be about \$0.5/L. Because the adsorption of dye in water was efficiently carried out without pH adjustment and the adsorbents were simply separated by the external magnet, no solvent was involved in the

recycling process. Therefore, the presented NiFe-LDO was assumed to be an efficient and cost effective adsorbent for adsorption of anionic dyes in strong acidic solution. The NiFe-LDH, the NiFe-LDO precursor was successfully prepared by the hydrothermal reaction; however, the use of synthetic chemicals was still the limitation of green synthesis; thus, the usage of natural extract (instead of urea and trisodium citrate) may be an optional study [40,41], which is a cost saving- and environmental-friendly method.

CONCLUSIONS

NiFe-layered double oxide was successfully prepared by the calcination of NiFe-layered double hydroxide at 400 °C for 120 min. The increase in the specific surface area, as well as saturation magnetization of the calcined products was due to the evaporation of the interlayer carbonate and water, as well as the synergistic effect of spinel NiFe₂O₄, respectively. The adsorption process was favorably spontaneous and pseudo-second-order reaction. The amounts of Congo red dye were almost removed by adsorbing onto NiFe-layered double oxide via the electrostatic and hydrogen-bonding interactions based on the q_m of 250 and 300 mg/g in the aqueous single dye and multiple dyes solution, respectively. The negative-charge and hydrogen-bonding sites play an important role on the adsorption of the dyes. The potential NiFe-LDO adsorbent can be reused for four times with 10% decrease of the dye removal efficiency in the mixture solution, indicating high adsorption performance and stability.

AVAILABILITY OF DATA AND MATERIALS

All data generated or analyzed during this study are included in the manuscript.

AUTHORS CONTRIBUTIONS

Sonchai Intachai supervised the research, analyzed and characterized the data, and took the lead in writing, editing the manuscript. Sonchai Intachai, Pornnapa Tongchoo and Prakaidao Pankam have carried out the experiments. Sonchai Intachai, Panita Sumanatrakul and Nithima Khaorapapong contributed to the interpretation of the results and revision of the manuscript.

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COMPETING INTERESTS

The authors declare no conflict of interest.

ETHICS DECLARATIONS

Ethics approval and consent to participate

Not applicable

Consent for Publication

The authors have consent to publish.

SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at <http://www.springer.com/chemistry/journal/11814>.

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Supporting Information

Efficient and practical adsorption of mixed anionic dyes in aqueous solution by magnetic NiFe-layered double oxide

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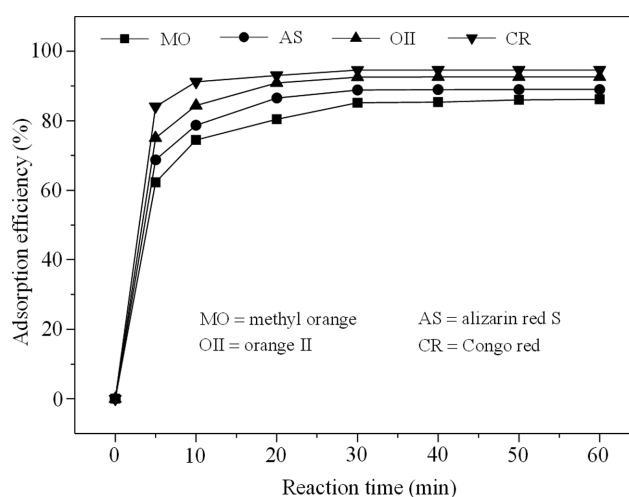


Fig. S1. Adsorption efficiency of mixed dyes onto NiFe-LDH.

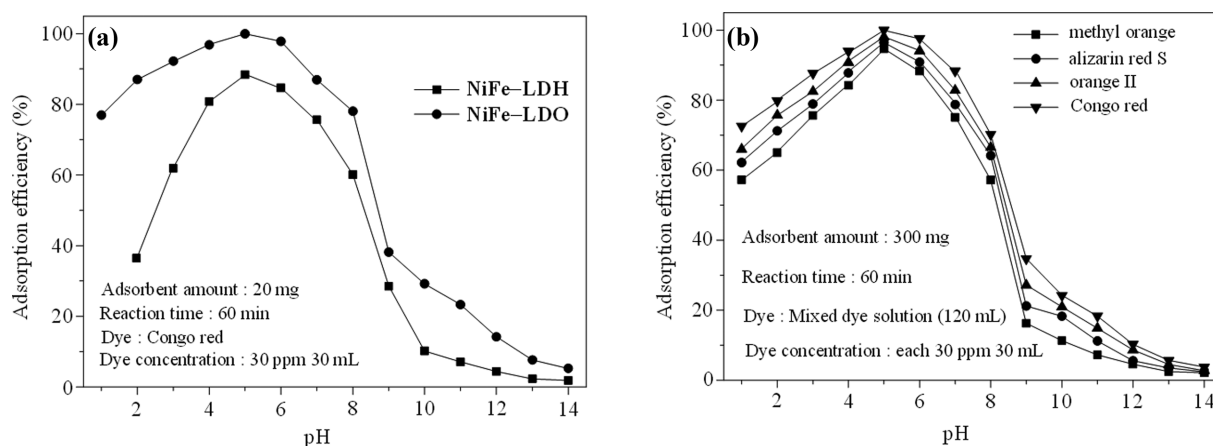


Fig. S2. Adsorption efficiency of (a) single dye onto NiFe-LDH and NiFe-LDO, and (b) mixed dyes onto NiFe-LDO at pH=1-14.

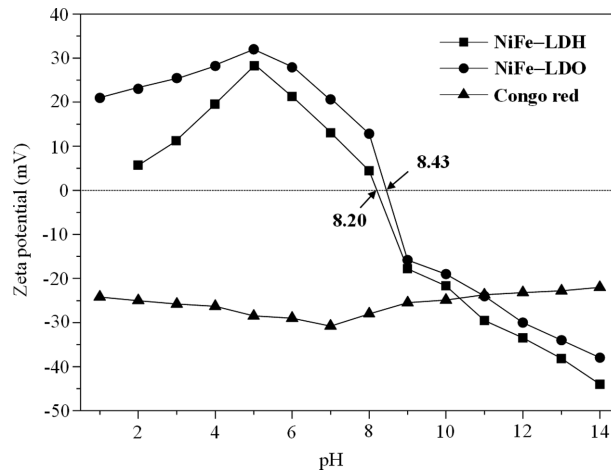


Fig. S3. Zeta potential of NiFe-LDH and NiFe-LDO dispersed in aqueous solution and Congo red solution at pH=1-14.

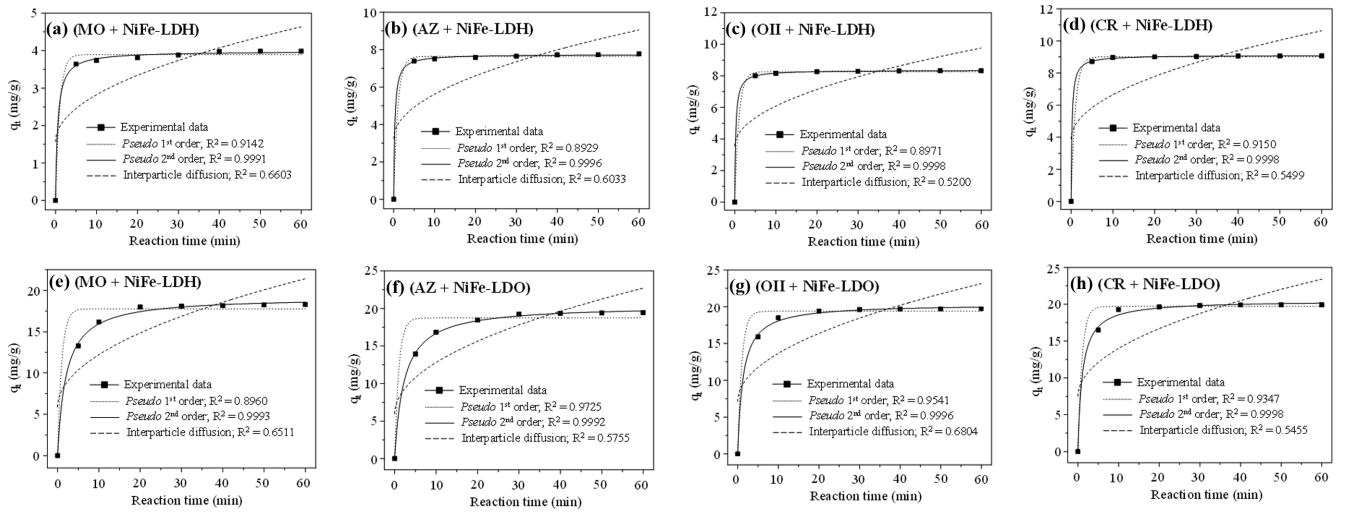


Fig. S4. Adsorption kinetics of single dye fitted by non-linear pseudo-first-order, pseudo-second-order and intraparticle diffusion models of (a)-(d) NiFe-LDH and (e)-(h) NiFe-LDO.

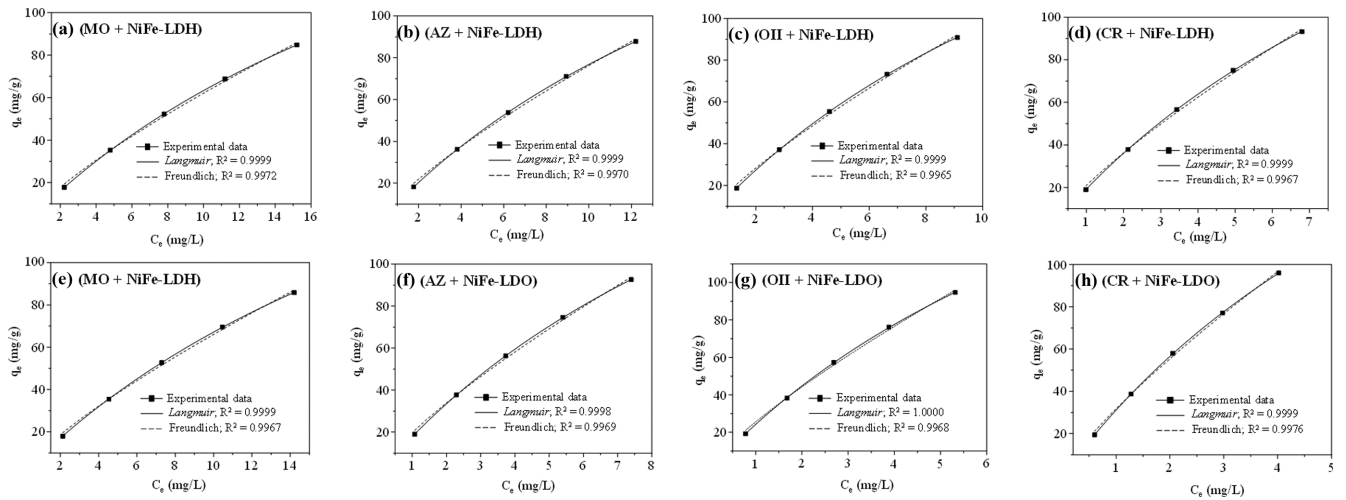


Fig. S5. Adsorption isotherms of single dye fitted by non-linear Langmuir and Freundlich models of (a)-(d) NiFe-LDH and (e)-(h) NiFe-LDO.

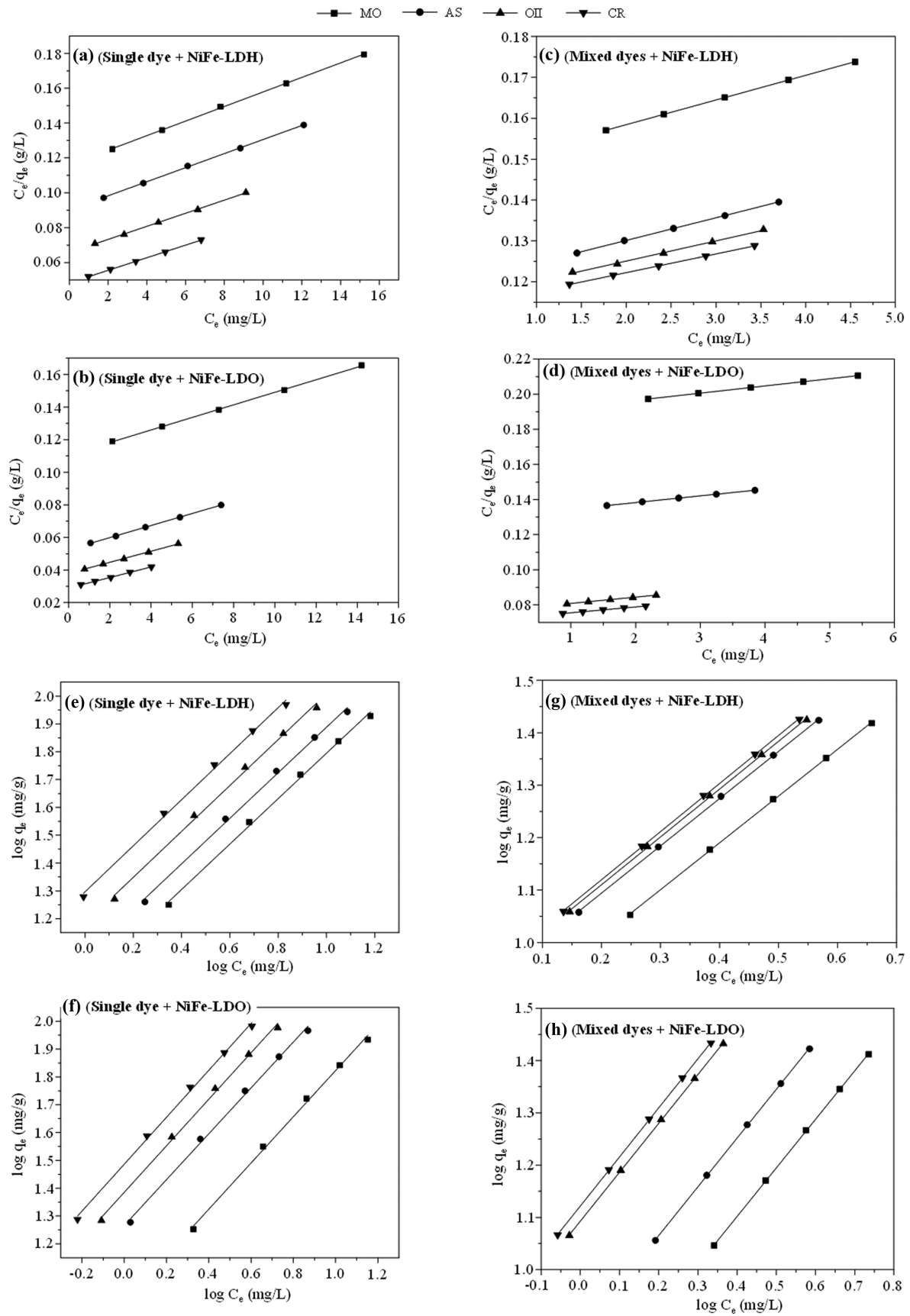


Fig. S6. Adsorption isotherms of single dye and mixed dyes fitted by linear Langmuir model of ((a) and (c)) NiFe-LDH and ((b) and (d)) NiFe-LDO, and by linear Freundlich model of ((e) and (g)) NiFe-LDH and ((f) and (h)) NiFe-LDO.

Table S1. Equations of the adsorption isotherms, and kinetics and thermodynamics

Model	Equation
Adsorption efficiency (%)	$\frac{(C_0 - C_t)}{C_0} \times 100$
Removal capacity at equilibrium, q_e (mg/g)	$\frac{(C_0 - C_e)}{m} \times V$
Removal capacity at any time, q_t (mg/g)	$\frac{(C_0 - C_t)}{m} \times V$
Pseudo-first-order kinetic	$q_t = q_e(1 - e^{-K_1 t})$
Pseudo-second-order kinetic	$q_t = \frac{q_e^2 K_2 t}{1 + q_e K_2 t}$
Intraparticle diffusion model	$q_t = K_i(t^{0.5}) + c$
Langmuir isotherm (Linear fitting)	$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{(K_L)(q_m)}$
Langmuir isotherm (non-linear fitting)	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$
Freundlich isotherm (Linear fitting)	$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e$
Freundlich isotherm (non-linear fitting)	$q_e = K_F C_e^{1/n}$
van't Hoff equation	$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$
Gibbs free energy equation	$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$

Where C_0 , C_t and C_e (mg/L) are the concentration of the aqueous dye solution at initial time, different “t” time and equilibrium, respectively, q_t (mg/g) and q_e (mg/g) are adsorption capacity at any time and equilibrium, respectively, m (g) is the mass of the adsorbent, V (L) is the volume of the aqueous dye solution. For the parameters, k_1 (min^{-1}) and k_2 (g/mg·min) are the pseudo-first-order and pseudo-second order rate constants, respectively, k_i is the intraparticle diffusion rate constant (mg/g·min^{1/2}), q_m (mg/g) is the maximum adsorption capacity, K_L (L/mg) is Langmuir adsorption equilib-

rium constant, $1/n$ is the heterogeneity factor, K_F ((mg/g)(L/mg)^{1/n}) is Freundlich constant and c is the intercept.

The thermodynamic data, including the change in enthalpy (ΔH ; kJ/mol), entropy (ΔS ; kJ/mol·K) and Gibbs free energy (ΔG ; kJ/mol), were determined from the adsorption data at three different temperatures (303, 323 and 343 K), where K_c (L/mg) is the distribution coefficient for adsorption, R is gas constant (8.314 J/mol·K) and T is absolute temperature (K, Kelvin).

Table S2. The adsorption parameters of single dye and mixed (M-) dyes in water that obtained by non-linear fitting model

Dye	Sample	Pseudo first order			Pseudo second order			Intraparticle diffusion			Langmuir isotherm			Freundlich isotherms		
		q_e (mg/g)	K_1 (min^{-1})	R^2	q_e (mg/g)	K_2 (g/mg·min)	R^2	K_i (mg/g min ^{1/2})	c	R^2	q_m (mg/g)	K_L (L/mg)	R^2	n	K_F (mg/g)· (L/mg) ^{1/n}	R^2
MO	NiFe-OII LDH CR	13.85	0.2569	0.9142	14.70	0.0329	0.9991	1.5066	4.4479	0.6603	242.2	0.0354	0.9999	1.29	10.4	0.9972
AS		14.65	0.2994	0.8929	15.23	0.0425	0.9996	1.5454	5.1329	0.6033	251.7	0.0440	0.9999	1.29	12.8	0.9970
OII		14.83	0.3860	0.8971	16.23	0.0561	0.9998	1.5733	5.8126	0.5200	262.4	0.0583	0.9999	1.29	16.2	0.9965
CR		18.01	0.3980	0.9150	18.60	0.0791	0.9998	1.8692	6.8558	0.5499	274.7	0.0756	0.9999	1.28	21.1	0.9967
MO	NiFe-OII LDO CR	17.77	0.2531	0.8960	19.20	0.0218	0.9993	2.0513	2.8744	0.6511	256.5	0.0354	0.9999	1.27	10.8	0.9967
AS		18.73	0.2657	0.9725	20.42	0.0268	0.9992	2.0661	5.9782	0.5755	268.6	0.0711	0.9998	1.28	19.7	0.9969
OII		19.38	0.3271	0.9541	21.36	0.0384	0.9996	2.1064	7.1825	0.6804	290.3	0.0912	1.0000	1.26	25.6	0.9968
CR		19.71	0.3559	0.9347	22.52	0.0461	0.9998	2.1598	7.5183	0.5455	308.0	0.1123	0.9999	1.25	31.8	0.9976
M-MO	NiFe-M-OII LDH M-CR	3.65	0.2830	0.9716	3.85	0.0909	0.9994	0.3992	1.2383	0.6309	165.9	0.0407	1.0000	1.13	6.86	0.9995
M-AS		7.31	0.3225	0.9926	7.56	0.1354	0.9995	0.7645	2.7575	0.5601	181.3	0.0412	1.0000	1.12	8.25	0.9997
M-OII		7.82	0.3930	0.9878	8.16	0.1514	0.9997	0.8330	2.8084	0.5913	199.4	0.0436	0.9998	1.11	8.53	0.9992
M-CR		8.50	0.4424	0.9672	8.73	0.1680	0.9999	0.8609	3.4079	0.5082	217.6	0.0463	1.0000	1.10	8.67	0.9998
M-MO	NiFe-M-OII LDO M-CR	3.89	0.5261	0.7739	3.99	0.4718	0.9998	0.3956	1.5720	0.5083	244.4	0.0217	1.0000	1.08	5.41	0.9998
M-AS		7.64	0.6624	0.9087	7.74	0.4912	0.9997	0.7490	3.2483	0.4582	264.3	0.0290	1.0000	1.08	7.60	0.9996
M-OII		8.26	0.6671	0.8789	8.36	0.5170	1.0000	0.8018	3.5513	0.4458	282.0	0.0458	1.0000	1.07	12.41	0.9997
M-CR		9.04	0.6675	0.7897	9.11	0.5194	1.0000	0.8707	3.8929	0.4402	299.9	0.0462	1.0000	1.07	13.27	0.9997

Table S3. The adsorption parameters of single dye and mixed (M-) dyes in water that obtained by linear fitting model

Dye	Sample	Langmuir isotherm		Freundlich isotherm		
		q_m (mg/g)	R^2	n	K_F (mg/g)·(L/mg) ^{1/n}	R^2
MO	NiFe-LDH	238.1	0.9996	1.23	9.53	0.9977
AS		250.0	0.9996	1.22	11.75	0.9976
OII		263.2	0.9995	1.21	15.27	0.9972
CR		277.8	0.9998	1.21	19.80	0.9975
MO	NiFe-LDO	256.4	0.9997	1.20	9.83	0.9975
AS		270.3	0.9999	1.21	18.45	0.9974
OII		294.1	0.9994	1.20	24.28	0.9977
CR		312.5	0.9993	1.19	30.6	0.9978
M-MO	NiFe-LDH	165.5	1.0000	1.12	6.80	0.9984
M-AS		181.0	1.0000	1.11	8.20	0.9981
M-OII		194.9	0.9998	1.10	8.50	0.9985
M-CR		218.3	0.9999	1.08	8.63	0.9982
M-MO	NiFe-LDO	243.9	0.9998	1.08	5.38	0.9985
M-AS		264.2	0.9999	1.07	7.56	0.9984
M-OII		282.0	1.0000	1.07	12.38	0.9983
M-CR		300.1	1.0000	1.06	13.24	0.9981

Table S4. Thermodynamic data of the adsorptive removal of mixed (M-) dyes in water

Dye	Adsorbent	Thermodynamic data	
		ΔH° (KJ/mol)	ΔS° (mol/KJ·K)
M-MO	NiFe-LDH	14.54	0.0655
M-AS		17.13	0.0738
M-OII		18.87	0.0790
M-CR		6.70	0.0375
M-MO	NiFe-LDO	19.00	0.0845
M-AS		19.98	0.0869
M-OII		10.90	0.0553
M-CR		10.92	0.0540

Table S5. Gibbs free energy data and efficiency of the adsorptive removal of mixed (M-) dyes in water

Dye	Adsorbent	Temperature (K)	ΔG° (KJ/mol)	Removal efficiency (%)
M-MO		303	-5.31	78.9
M-AS			-5.23	82.5
M-OII			-5.06	87.4
M-CR			-4.66	90.1
M-MO	NiFe-LDH	323	-6.62	83.8
M-AS			-6.71	86.3
M-OII			-6.64	91.5
M-CR			-5.41	93.6
M-MO		343	-7.94	91.3
M-AS			-8.19	94.7
M-OII			-8.22	97.2
M-CR			-6.16	98.6
M-MO		303	-6.55	89.8
M-AS			-6.35	91.7
M-OII			-5.85	94.1
M-CR			-5.45	96.4
M-MO	NiFe-LDO	323	-8.23	95.2
M-AS			-8.09	96.3
M-OII			-6.99	98.3
M-CR			-6.54	99.4
M-MO		343	-9.92	98.1
M-AS			-9.82	99.2
M-OII			-8.06	100
M-CR			-7.62	100