



Short Communication

Preparation and utilization of Keggin-type polyoxometalate intercalated Ni–Fe layered double hydroxides for enhanced adsorptive removal of cationic dye

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Abstract

The Ni–Fe layered double hydroxide (LDH) intercalated by Keggin-type polyoxometalate (POM) of $\text{SiW}_{12}\text{O}_{40}^{4-}$ was investigated for the first time. The synthesized Ni–Fe LDH and Ni–Fe POM were characterized by XRD, FT-IR, and N_2 adsorption–desorption isotherm to identify the intercalation process as well as their surface morphology. The obtained results indicated that after intercalated by POM, the interlayer distance of the LDH expanded due to the insertion of POM anion and removal of some native NO_3^- anion in the interlayer space. Moreover, the increment of the BET surface area of the material after intercalation indicated the opening of the interlayer space that beneficial for the adsorption process. The study on the malachite green adsorption onto the synthesized materials showed that POM intercalated LDH has better adsorption capacity than the original LDH, where the adsorption kinetic was better described by pseudo second order model than the pseudo first order model.

Keywords Ni–Fe LDH · Polyoxometalate · Intercalation · Adsorption · Malachite green

1 Introduction

Dye contaminated water resource due to textile industry activities has gained considerable attention in recent decades. It was estimated that around 100 tons of dyes were discharged into the water body annually due to the lack of dyeing process efficiency [1]. Since it has a detrimental effect to the living organism, numerous attempts have been developed to remove dyes from industrial wastewater [2]. Among the established methods, adsorption is still considered as the most feasible and affordable methods for treating the dye contaminated wastewater. Moreover, the availability of the various adsorbents, such as activated carbon, clays and clay minerals, zeolite, layered double hydroxides (LDHs), and even agricultural wastes,

has increased the appealing of this method for further development [3].

LDH, a synthetic clay with positively charged surfaces, is considered as one of the most potential adsorbents for dyes removal since it can be easily fabricated and exhibited high anion exchange characteristics [4]. However, its applicability may not live up to all kinds of dyes since it has deficient adsorption capacity to cationic dyes [5]. Therefore, LDH modification by means of composites or intercalation has been widely conducted in order to enhance their adsorption capability. Polyoxometalate (POM) has long been considered as the ideal pillaring agent since it has a robust structure and possesses a wide range of charge density; thus, it will impart a large gallery high [6].

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Although POM intercalated LDH has been widely investigated, the study on the use of Ni–Fe LDH as the starting material is still limited. Recently, Thenuwara et al. [7] used cobalt to enhance to inter gallery high of Ni–Fe LDH, and they found that the interlayer spacing increased from 7.98 to 8.29 Å. In this work, we have tried to utilize Keggin POM, namely $\alpha\text{-SiW}_{12}\text{O}_{40}^{4-}$ to intercalate Ni–Fe LDH that synthesized by facile co-precipitation method. The obtained products were further employed as an adsorbent for cationic dye (malachite green) removal from aqueous solution.

2 Experimental

2.1 Synthesis of Ni–Fe LDH

The original Ni–Fe LDH was synthesized by following the previously reported procedure by Choudary et al. [8] using a simple co-precipitation method. Briefly, 70 mL of the aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.10 mol) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.05 mol) was added slowly into a beaker flask containing 100 mL of NaOH (0.3 mol) and Na_2CO_3 (0.094 mol) solution under vigorous stirring at room temperature. After finished, the obtained suspension was allowed to age at 65 °C for 18 h. Afterward, the obtained solid was cooled down in the room temperature, then rinsed with distilled water three times and dried at 80 °C overnight.

2.2 Preparation of Ni–Fe POM

Keggin-type polyoxometalate intercalated Ni–Fe LDH was prepared using the ion-exchange route by following the previously reported paper [9]. In brief, 0.1 g of Ni–Fe LDH powder was dispersed into 100 mL of $\text{K}_4\alpha\text{-SiW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$ solution (10 mmol/L). The mixture was then stirred vigorously at 60 °C under nitrogen atmospheric condition for 3 h. The obtained material was separated, rinsed, and dried at 80 °C overnight, and the final product was labeled as Ni–Fe POM.

2.3 Materials characterization

X-ray diffraction patterns were recorded using Rigaku Miniflex 600 X-ray diffractometer with Ni filtered CuK α irradiation. The samples were scanned from 2θ angle range 5°–80°. FT-IR spectra were recorded using a Shimadzu Prestige-21 FTIR instrument with the KBr disc method. The surface morphology of the samples was studied by N_2 adsorption–desorption isotherm using ASAP 2020–Physorption instrument from Micromeritics.

2.4 Adsorption studies

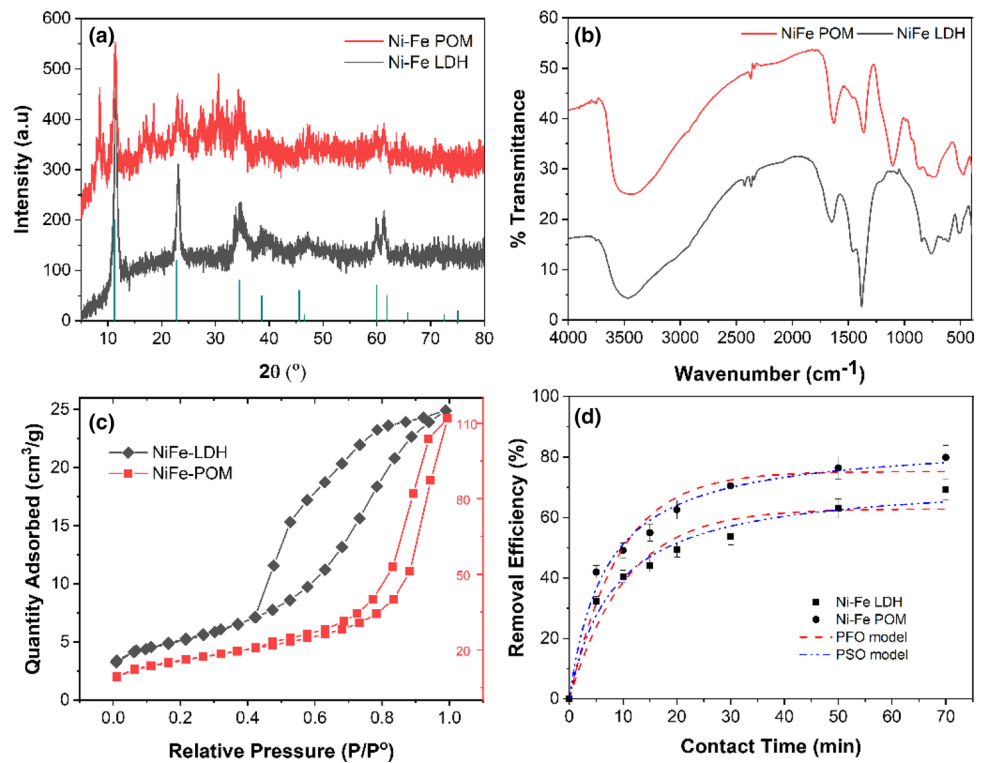
The adsorption study was conducted using malachite green (MG) as the model of dye-containing wastewater. The adsorption process was studied in a batch method with the constant adsorbent amount, while the other operational parameters were varied. The mixture of adsorbent and dye solution was mixed with a constant stirring speed of 400 rpm for a predetermined time, and the remaining dye concentration was analyzed by UV–vis spectrophotometry method. The parameter of adsorption kinetics was calculated according to its mathematical equation provided in the literature [10].

3 Results and discussion

The powder X-ray diffraction patterns of the starting material Ni–Fe LDH and the intercalated Ni–Fe POM are shown in Fig. 1a. The XRD pattern of Ni–Fe LDH showed three symmetrical peaks at the low 2θ value and asymmetric peaks at a higher 2θ value. The presence of these symmetric peaks as well as the doublet peak at 2θ value of c.a. 60° is an indication that the tested material has a well-ordered layer structure [11]. Moreover, the recorded XRD pattern of the starting Ni–Fe LDH fit well with standard JCPDS no. 22-0700, which indicated that the material has a similar structure as hydrotalcite. The interlayer distance of Ni–Fe LDH can be determined from the peak with the lowest 2θ value that corresponds to the (003) reflection [12]. After intercalated by POM anion, it can be observed that the (003) reflection peaks shifted to the lower 2θ value. It can be calculated that after intercalated by POM, the interlayer distance of Ni–Fe POM increased from 7.71 to 10.38 Å. The interlayer distance enlargement evidenced that some of the native interlayer anions of Ni–Fe LDH were successfully replaced by POM anion, as also reported by Ma et al. [9].

Next, the FT-IR spectra of Ni–Fe LDH and Ni–Fe POM are displayed in Fig. 1b. The broad and strong band at 3465 cm^{-1} and 1650 cm^{-1} were assigned to the stretching and bending vibration of –OH group that belongs to the interlayer water molecule as well as hydroxyl surface group of LDH. Moreover, it can be noted that the FT-IR spectra of Ni–Fe LDH exhibited a strong band at 1379 cm^{-1} that assigned to the N–O stretching band of NO_3^- anion as the native anion in the interlayer space of LDH [13, 14]. Several peaks that emerged below 1000 cm^{-1} were related to the vibrational mode of M–O/O–M–O, where M refers to the metal cation of Ni^{2+} or Fe^{3+} [15]. After intercalated by $\text{SiW}_{12}\text{O}_{40}^{4-}$, it can be

Fig. 1 XRD pattern (a), FT-IR spectra (b), N₂ adsorption–desorption properties (c), and removal efficiency (d) of the prepared materials



observed that the band corresponding to the existence of NO₃⁻ anion was significantly reduced. This finding indicated that almost all NO₃⁻ anion in the interlayer space of LDH was successfully removed and changed by SiW₁₂O₄₀⁴⁻. Furthermore, a new vibration band emerged at 1103 cm⁻¹ that assigned to Si–O vibration indicated the existence of POM anion in the interlayer of LDH.

The textural properties of Ni–Fe POM and Ni–Fe LDH that assessed by N₂ adsorption–desorption isotherm can be seen in Fig. 1c. Both materials showed a similar isotherm type, i.e., type IV, that confirmed the existence of mesopore [15]. The specific surface area of the materials was then determined by the BET method. After intercalated by SiW₁₂O₄₀⁴⁻, the surface area of Ni–Fe LDH

increased from 18.25 to 56.62 m²/g. This finding probably caused by the interlayer opening due to the existence of POM anion. Moreover, for the adsorption purpose, the higher the surface area of the used adsorbent, the more adsorption site available that can increase dye uptake.

The effect of contact time on the adsorption of MG into both synthesized materials are displayed in Fig. 1d. By increasing the adsorption time, the dye removal efficiency gradually increased until it reached its equilibrium time at c.a. 70 min with the equilibrium adsorption capacity (*q_e*) of 6.93 and 7.99 mg/g for Ni–Fe LDH and Ni–Fe POM, respectively. The obtained data were then simulated two kinetic models, namely pseudo first order (PFO) pseudo second order (PSO), where the obtained plot of

Fig. 2 Linear equation plot of PFO (a) and PSO (b) models

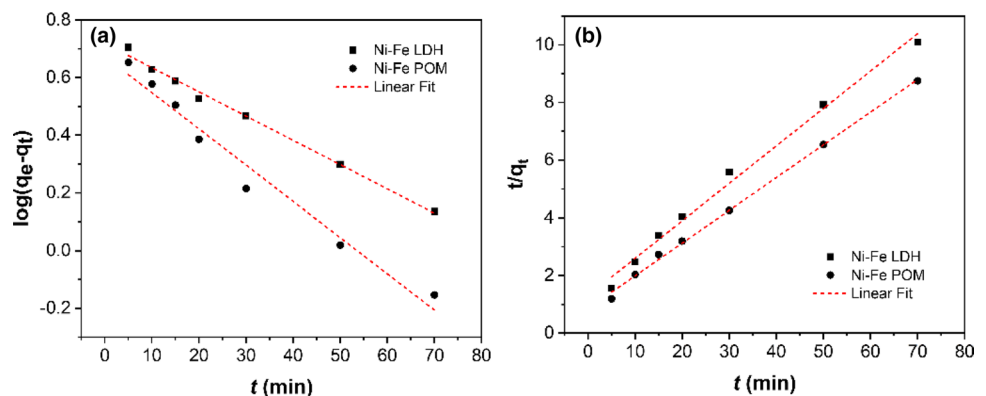


Table 1 PFO and PSO kinetic models' parameters for MG adsorption

Kinetics model	Parameters	Ni-Fe LDH	Ni-Fe POM
PFO	$q_{e,cal}$ (mg/g)	5.2345	4.7136
	k_1 (1/min)	0.0193	0.0289
	R^2	0.9937	0.9730
PSO	$q_{e,cal}$ (mg/g)	7.7021	8.8114
	k_2 (g/mg min)	0.0129	0.0150
	R^2	0.9915	0.9978

their linear equation, as well as the results of the kinetic parameters, are arranged in Fig. 2 and Table 1, respectively. Based on the obtained correlation coefficient value (R^2), it can be concluded that the adsorption kinetic was better described by the PSO model rather than the PFO model since the PSO model produced higher R^2 value [16]. Moreover, the obtained equilibrium adsorption capacity (q_e) implied that after intercalation, Ni-Fe POM exhibited better adsorption capacity than the original Ni-Fe LDH.

4 Conclusion

Ni-Fe LDH was successfully intercalated by $\text{SiW}_{12}\text{O}_{40}^{4-}$ polyoxometalate by facile ion exchange method under the nitrogen atmospheric condition. The obtained materials (Ni-Fe POM) exhibited higher interlayer distance as well as a specific surface area than the original Ni-Fe LDH. Application of both materials for adsorptive removal of malachite green (MG) showed that the equilibrium adsorption capacity of Ni-Fe LDH and Ni-Fe POM was 6.93 and 7.99 mg/g, respectively. The adsorption kinetic study revealed that the MG uptake was better described by the pseudo second order model than the pseudo first order model.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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