

Zinc–aluminum layered double hydroxide as a nano-sorbent for removal of Reactive Yellow 84 dye from textile wastewater effluents

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Abstract In this research, the zinc–aluminum layered double hydroxide (Zn–Al LDH) was synthesized and structurally and morphologically characterized by X-ray diffraction, Fourier transform infrared spectroscopy, transmission electron microscopy and N_2 adsorption–desorption techniques. The obtained nano-structured inorganic material was employed as an innovative nano-sorbent for separation of Reactive Yellow 84 (RY84) dye from aqueous solutions, which can be spectrophotometrically monitored at $\lambda = 359$ nm. The effect of several parameters such as type of interlayer anion in Zn–Al LDH structure, pH, sample flow rate, elution conditions, amount of nano-sorbent, sample volume and co-existing ions on the retention efficiency was investigated and optimized. The results showed that trace amounts of the RY84 could be retained using a column packed with 300 mg of the Zn–Al(NO_3^-) LDH at pH 8 and stripped by 2.5 mL of 3.0 mol L^{-1} NaOH. Under the optimum experimental conditions, the limit of detection and the relative standard deviation were $0.04 \text{ } \mu\text{g mL}^{-1}$ and 1.8 %, respectively. The calibration graph using the presented solid phase extraction system was linear in the range of $0.15\text{--}1.5 \text{ } \mu\text{g mL}^{-1}$ with a correlation coefficient of 0.9982. The method was successfully applied to removal of RY84 from several textile wastewater effluents.

Keywords Reactive Yellow 84 dye · Zinc–aluminum layered double hydroxide · Nano-sorbent · Solid phase extraction · Textile wastewater samples

Introduction

Controlling pollution is the main concern of environmental scientists today. Synthetic dyes are extensively used in textile dyeing, paper, printing, color, photography, pharmaceuticals, cosmetics and other industries [1]. Approximately, 10–15 % of the dyes are released into the environment during dyeing process and released in the textile effluents [2]. Textile dyes are potentially toxic because they are difficult to be treated by the conventional wastewater treatment systems and if untreated would cause long-term health concerns [3]. On the other hand, the effluent from the dyeing processes is characterized by a low biodegradability. In recent years, reactive dyes have been most commonly used due to their advantages such as better dyeing processing conditions and bright colors. Generally, reactive dyes contain functional groups such as azo, anthraquinone, phthalocyanine, formazin, and oxazin as chromophore. Among the reactive dyes, approximately, 66 % are azo dyes [4]. Reactive dyes are both highly water soluble due to high degree of sulfonation and non-degradable under typical aerobic conditions found in conventional biological treatment systems [5]. Various chemical and physical processes are currently in use for the removal of dyes by conventional treatment technologies including biological and chemical oxidation, chemical coagulation, foam flotation, electrolysis, biodegradation, advanced oxidation, photocatalysis, electrochemical methods, but often suffer from economic point of view [6–17]. Solid phase extraction (SPE), however, is an

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effective method and could be used for the selective extraction of dyes from aqueous solutions. Different types of mineral or organic sorbents such as silica beads, activated carbon, zeolites, polyamines beads, polyurethane resins, gels, calixarenes, and chitosan have been employed in SPE procedures [18–21].

Layered double hydroxides (LDHs) have been recently introduced by our research group as a new class of nano-sorbents in SPE of some anions from aqueous solutions [22–27]. LDHs have been applied as anion exchangers, adsorbents, medicine stabilizers, catalysts, solid-state nano-reactors, polymer composites, and bioactive materials [28–34]. The extensive applications of the LDHs may be partially understood as being related to the special layered structure and the replaceable ions in composition. The general formula of the LDHs is $[M_{1-X}^{2+} M_X^{3+}(\text{OH})_2]^{b+} [A^{n-}]_{b/n} \cdot m\text{H}_2\text{O}$, where M^{2+} and M^{3+} are the divalent and trivalent cations in the octahedral positions within the hydroxide layers, A^{n-} is an interlayer anion with a negative charge n , and b is the charge of the layer and m is the number of water molecules. The anions in the interlayer of LDHs are exchangeable and the layered structure can incorporate a variety of anions. Therefore, they are regarded as prominent hosts of hybrid materials [35]. As mentioned above, due to LDH's permanent layer positive charge, high anion-exchange capacity, large surface area, good thermal stability, water resistant structure and rapid regeneration, LDHs are considered as a new class of green nano-sorbents for SPE of organic and inorganic anions [22–27].

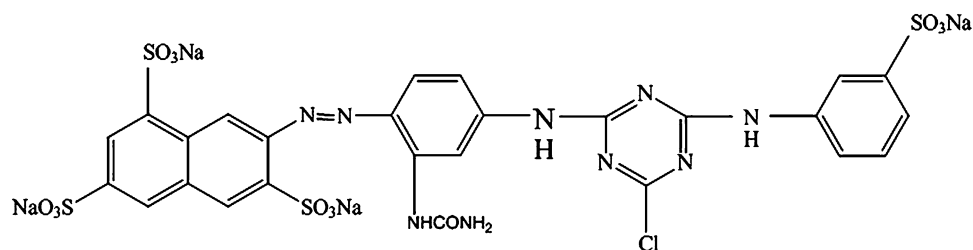
Although Zn–Al(NO_3^-) LDH has been recently used for extraction of phosphate from aqueous solutions by other researchers [36], no attempt has been made to apply the LDH in removal of organic pollutants such as pigments and dyes. Therefore, in this work, we have utilized the Zn–Al(NO_3^-) LDH as a nano-sorbent for removal of Reactive Yellow 84 (RY84) dye (Fig. 1) from textile wastewater effluents, which can be spectrophotometrically monitored at $\lambda = 359$ nm. The effects of several parameters on the retention efficiency of RY84 dye were systematically investigated and the presented method was successfully applied to the separation and determination of RY84 in several textile wastewater samples.

Experimental

Apparatus and instruments

A 1601PC UV–Vis spectrophotometer (Shimadzu, Japan) with a wavelength range of 200–800 nm was used for recording the spectra and measuring the absorbance. The instrument equipped with dual source lamp (Tungsten and deuterium for Vis and UV range, respectively), 1.0 cm quartz cell and Si-PD detector. The spectral bandwidth and response time were set at 2 nm and 0.2 s, respectively. A 2 mL polypropylene cartridge (30 mm \times 7 mm i.d.) (Shafa Co., Iran) packed with 300 mg of Zn–Al(NO_3^-) LDH and fitted with small polyester fibers at both ends to prevent material losses was used to pre-concentrate the analytes in SPE procedures. The flow rate of solution through the column was controlled with an air-driven fluid pump model P34112 (Taiwan). In order to structural study of the LDH, XRD measurements were performed on a Siemens D5000 X-ray powder diffractometer (Cu K_α radiation source, $\lambda = 0.154056$ nm) between 2° and 70° generated at 40 kV and 35 mA at room temperature. Samples for XRD were ground into powder and then pressed flat in the sample slot. In addition, FT-IR spectra ($4,000$ – 400 cm^{-1}) were recorded on a (Shimadzu 8400 series, Japan) Fourier transform infrared spectrometer using the KBr disk method with a ratio sample/KBr of 1:100 by mass. TEM image was obtained using a transmission electron microscope (TEM), model PHILIPS SM10 equipped with EPSON 8300 photo flat-bed scanner at an accelerating voltage of 150 keV. Nitrogen adsorption–desorption isotherms, surface area, pore-size distribution, and pore volume were determined by nitrogen adsorption–desorption measurements at 77 K using a BEISORP (BEL Japan, Inc.) analyzer and adsorption/desorption data analysis software version 6.1.0.4. The samples were degassed in vacuum at 373 K for 4 h prior to measurements. The BET surface area was determined by a multipoint BET method using the adsorption data in the relative pressure (P/P_0) range of 0.05–0.35. The pore-radius (r_p) distribution was analyzed by the Barrett–Joyner–Halenda (BJH) model using the adsorption branch of isotherms. The nitrogen-adsorption volume at the relative

Fig. 1 The chemical structure of Reactive Yellow 84 (RY84)



pressure of 0.990 was used to determine the pore volume (V_p) and average pore diameter. Electrical furnace model Ex.1200-30L (Exciton Co., Iran) and N_2 gas (99.9995 %, Azaroxide Co., Iran) were used in LDH preparation process. The pH values were measured with a Metrohm pH-meter (model 827), supplied with a glass-combined electrode. An electronic analytical balance (GR-200, Japan) was used for weighing the solid materials.

Standard solutions and reagents

All chemicals used were of analytical-reagent grade and all solutions were prepared with high purity deionized water (Shahid Ghazi Co., Tabriz, Iran). Stock solutions of RY84 ($1,000 \text{ mg L}^{-1}$) were prepared in deionised water and the solutions of lower concentrations were prepared by appropriately diluting the stock solutions with deionized water. All the solutions of RY84 were kept in amber color glassware throughout the experiment. The azo dye, RY84, was purchased from Alvan Sabet Co. (Iran) with 99 % purity. All salts used for the interference study, NaOH, and LDH precursors, i.e., purified zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 99 %), aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$, 99 %) were purchased from Merck (Darmstadt, Germany). The pipettes and vessels used for the trace analysis were kept in 15 % (v/v) nitric acid at least overnight, and subsequently washed three times with deionized water prior to use.

Preparation of zinc–aluminum layered double hydroxide

The $Zn-Al(NO_3^-)$ LDH was prepared using a co-precipitation method with controlled pH, and followed by thermal treatment. The synthesis was carried out under a N_2 atmosphere, and all the solutions were prepared using deionized water to avoid contamination. In the present work, the $Zn^{2+}:Al^{3+}$ molar ratio chosen for the synthesis of the LDH precursors was 2:1. For this purpose, 2.970 g $Zn(NO_3)_2 \cdot 6H_2O$ and 1.875 g $Al(NO_3)_3 \cdot 9H_2O$ were added into 30 mL of a water and ethanol mixture (1:1) under vigorous stirring at room temperature. The pH was adjusted to 9 ± 0.2 by the addition of 1 mol L^{-1} NaOH solution. Then, the obtained slurry was subjected to thermal treatment at a constant temperature of $60 \text{ }^\circ\text{C}$ for about 24 h. Afterward, the resulting precipitate was separated by centrifugation at 4,000 rpm for 10 min and washed three times with deionized water, and dried at $50 \text{ }^\circ\text{C}$ for 8 h.

Column preparation

The SPE column was prepared by introducing 300 mg of $Zn-Al(NO_3^-)$ LDH into an empty 2 mL polypropylene

cartridge using the dry packing method. Both ends of the column were plugged with a small portion of polyester fibers to retain the nano-sorbent in the column. Before loading the sample, the column was cleaned with 3 mL of 3 mol L^{-1} NaOH solution and conditioned by passing only 5 mL of deionized water through the column prior to each use.

Sample preparation

Several textile wastewaters were selected as real samples for analysis by the presented method. The samples were filtered through Black band filter paper to remove any suspended particulate. Then, aliquots of 150 mL of each sample were analyzed by following the procedure described in “General procedure” section.

General procedure

For extraction and determination of RY84 by SPE method, aliquots of 150 mL of aqueous standard or sample solution containing RY84 in the range of $0.15\text{--}1.5 \text{ } \mu\text{g mL}^{-1}$ (pH 8) were passed through the $Zn-Al(NO_3^-)$ LDH nano-sorbent in a column at a flow rate of 3 mL min^{-1} . After loading, the retained analyte on the column was eluted with 2.5 mL of 3 mol L^{-1} NaOH solution at an elution rate of 1 mL min^{-1} . The concentration of the RY84 was spectrophotometrically monitored by measuring the absorbance of the solution at $\lambda = 359 \text{ nm}$.

Results and discussion

Selection of layered double hydroxide

LDHs consist of positively charged hydrotalcite-like layer of metal hydroxide and the interlayer region typically occupied by anionic species and water molecules. Distance between the hydroxide layers forming ‘galleries’ can vary over a wide range. LDHs have relatively weak interlayer bonding and, consequently, various kinds of inorganic or organic anions could be introduced into the hydroxide interlayer by simple ion exchange reaction or surface adsorption. On the other hand, the charge density and the anion-exchange capacity of the LDHs may be controlled by varying the type of di- and tri-valent cations and their ratios in the LDH structure. Therefore, three LDHs with different divalent cations, i.e., Zn^{2+} , Ni^{2+} and Mg^{2+} were synthesized under the same conditions and used in SPE of RY84. Figure 2a displays the effect of LDH type, with NO_3^- interlayer anion, on retention of RY84. As it can be seen, the best result was achieved in the case of $Zn-Al$ LDH with (2:1) $Zn^{2+}:Al^{3+}$ molar ratio. Thus, $Zn-Al$ LDH could be

used as a nano-sorbent for SPE of RY84 from aqueous solutions. As mentioned above, type of interlayer anion is also important and can affect the retention efficiency owing to resulting interlayer space. Therefore, three Zn–Al LDHs with different interlayer anions such as Cl^- , NO_3^- and CO_3^{2-} were synthesized and tested for removal of RY84. As can be seen from Fig. 2b, the highest recovery was obtained in the case of NO_3^- interlayer anion and Zn–Al(NO_3^-) LDH was then used in further experiments.

Characterization of zinc–aluminum layered double hydroxide

A set of characterization was performed to get better insight into the structural properties of the sorption matrix, which has been used in this study as a solid phase extractor. The powder X-ray diffraction (XRD) is a very powerful technique for characterizing the structure of materials.

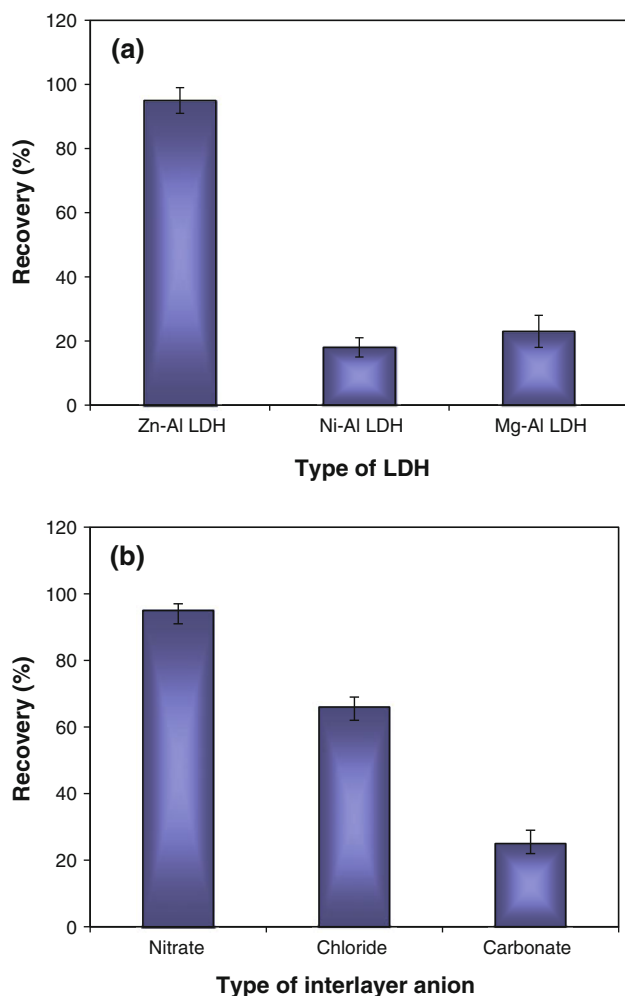


Fig. 2 Effect of LDH type with the same interlayer anion (a), and interlayer anion type, between the hydroxide layers in Zn–Al LDH nano-sorbent (b) on the retention of RY84

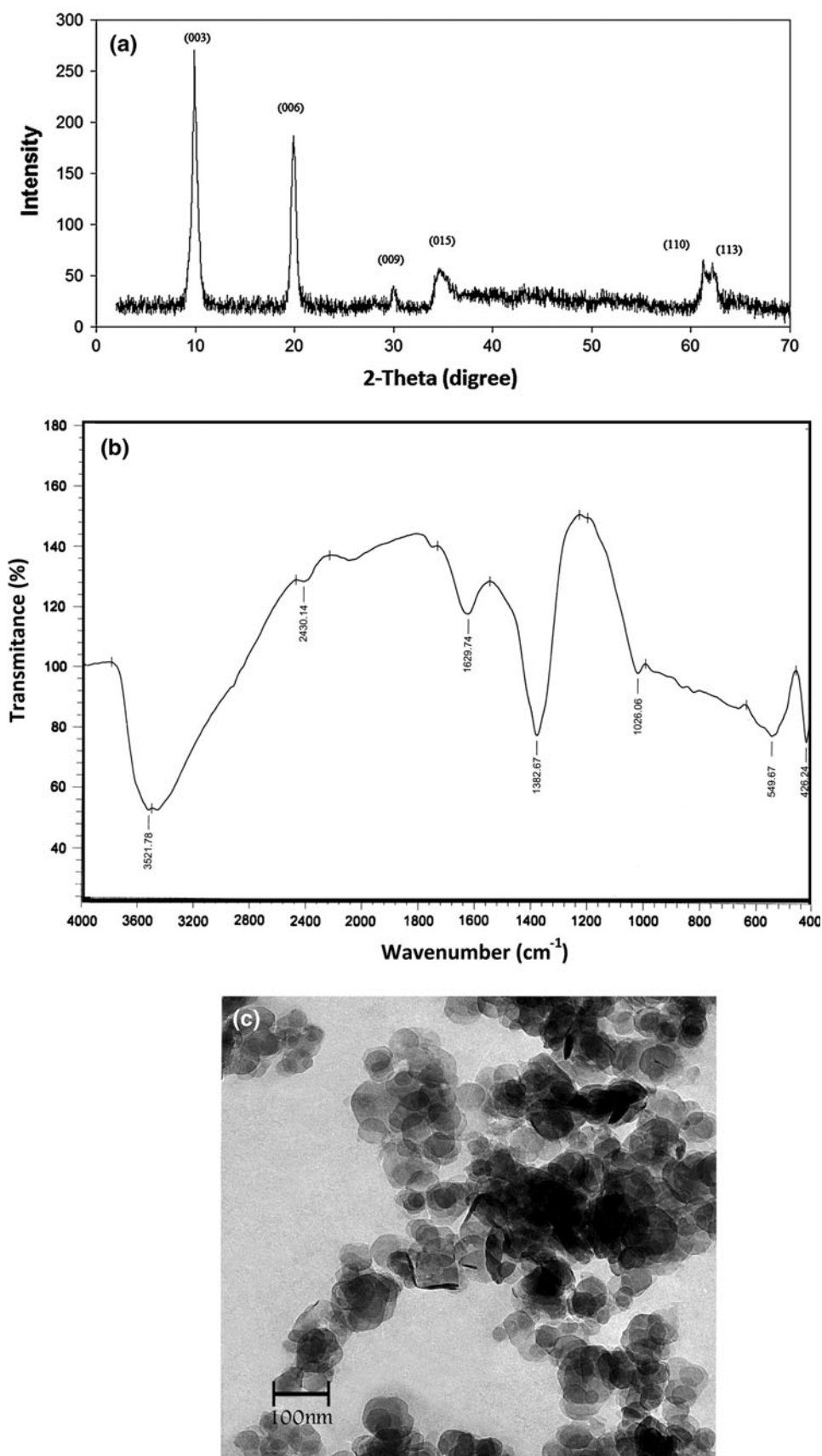
Figure 3a shows XRD pattern of Zn–Al(NO_3^-) LDH. It can be observed the characteristic reflections of (0 0 3) (0 0 6) (0 0 9), and (0 1 5) planes of a crystalline LDH. In the zone close to $2\theta = 61^\circ$ – 63° , the typical doublet of (1 1 0)–(1 1 3) planes of LDH was also observed. It can be seen that Zn–Al(NO_3^-) LDH exhibits the characteristic reflections of hydrotalcite-like LDH and no other crystalline phases were present. The infrared absorption spectroscopy was used to identify the nature and symmetry of interlayer anions and the presence of impurity phases. The absorption band around $3,521\text{ cm}^{-1}$ shown in the FT-IR spectrum of the Zn–Al(NO_3^-) LDH precursor (Fig. 3b) can be assigned to the stretching vibration of the hydroxyl groups of LDH layers and interlayer water molecules. The bending mode of water molecules is responsible for the weak band at $1,629\text{ cm}^{-1}$. The band with maximum peak at $1,382\text{ cm}^{-1}$ is attributed to stretching vibration of NO_3^- ions intercalated in the interlayer gallery. Finally, the bands at 543 and 426 cm^{-1} can be ascribed to M–O stretching modes and M–O–H bending vibrations. Transmission electron microscopy (TEM) was also employed to explore the morphology and distribution pattern of the nano-structured Zn–Al(NO_3^-) LDH (Fig. 3c). As can be seen, small tedious platelets of the LDH were dispersed homogeneously throughout the solution. Hence, the prepared LDH considered as a novel nano-sorbent for extraction of RY84 prior to determination by spectrophotometry.

The nitrogen adsorption–desorption isotherms of Zn–Al(NO_3^-) LDH samples with different $\text{Zn}^{2+}:\text{Al}^{3+}$ molar ratios and their corresponding pore-size distributions are shown in Fig. 4. As can be seen from Fig. 4a, the nitrogen adsorption–desorption isotherms are found to be of type IV according to the Brunauer–Deming–Deming–Teller (BDDT) classification and exhibited a H3 hysteresis loop at high relative pressure and also H2 hysteresis loop at low relative pressure, that is typical of mesoporous solid [37, 38]. The maximum adsorption of the nitrogen gas and specific surface area decreased with the increasing of $\text{Zn}^{2+}:\text{Al}^{3+}$ molar ratio from 2 to 3. The multimodal pore-size distributions are further confirmed by their corresponding pore-radius distribution curve as shown in Fig. 4b. The pore structure parameters of the studied samples such as the specific surface area, average pore-size and pore volume are listed in Table 1.

Optimization of solid phase extraction conditions

To obtain the most suitable data from this SPE system, different parameters such as amount of LDH, pH of sample solution, the type and concentration of eluent, the effect of sample and eluent flow rates on the extraction efficiency were studied and optimized. The optimization procedure was carried out by varying a parameter while the others

Fig. 3 **a** XRD pattern, **b** FT-IR spectrum, and **c** TEM image of Zn-Al(NO_3^-) LDH



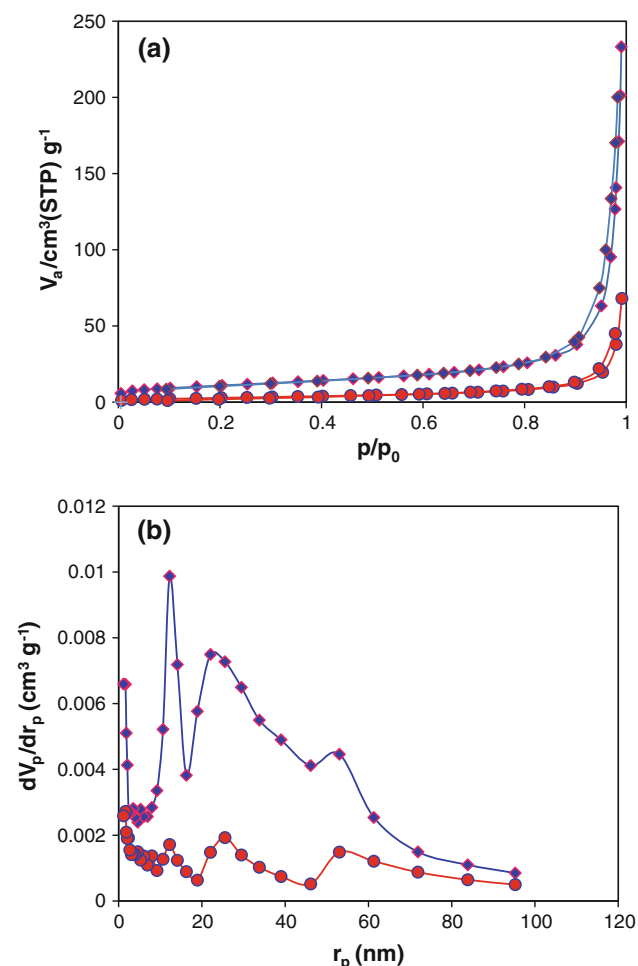


Fig. 4 **a** Nitrogen adsorption-desorption isotherms, and **b** pore-size distribution curves of the Zn–Al(NO₃[−]) LDHs with Zn²⁺:Al³⁺ molar ratios of 2:1 (filled diamond) and 3:1 (filled circle)

Table 1 Physico-chemical properties of the Zn–Al(NO₃[−]) LDH samples

Samples	Molar ratio (Zn ²⁺ :Al ³⁺)	Average pore-size (nm)	Pore volume (cm ³ g ^{−1})	Specific surface area (m ² g ^{−1})
Zn ₂ –Al(NO ₃ [−]) LDH	2:1	35.584	0.3481	39.131
Zn ₃ –Al(NO ₃ [−]) LDH	3:1	36.211	0.0986	10.897

were kept constant. A 0.8 μg mL^{−1} of RY84 solution was used for all the measurements and three independent experiments were carried out for each optimized variable. The recovery percentage, which was calculated from the amount of RY84 in the starting sample and the amount of RY84 eluted from the column, used as the analytical signal.

Effect of pH

In the SPE studies, pH is the first important factor for the quantitative recoveries of analytes. The effect of pH on the recovery of RY84 was investigated in the range of 4–12, and the results were shown in Fig. 5. It can be seen that the retention of RY84 depends on the pH of the sample solution and the optimum pH range was around 6–9. At pH < 4, the uptake capacity was low due to dissolution of the layered materials in strong acidic media. For pH < pH_{pzc}, the LDH surface is positively charged, favoring adsorption of the RY84. As the pH approached that corresponding to the pH_{pzc} of LDH, the surface charge decreased resulting in reduced RY84–LDH interactions leading to low RY84 uptake. Keeping the pH in the range between 6 and 9 facilitated electrostatic interactions between LDH layers and RY84 [39, 40]. An increase in the concentration of the competing OH[−] anions at pH above 9.0 might be responsible for the observed decrease in the recovery at higher pH. According to the obtained results, pH 8 was selected for subsequent experiments, and buffer solution was not employed for pH adjusting of the standard solutions and/or real samples because of the wide optimum pH range.

Effect of sample loading flow rate

The influence of RY84 retention on nanometer-sized Zn–Al(NO₃[−]) LDH was investigated by varying the flow rate of the sample solution in the range of 0.5–5 mL min^{−1} through the packed column using an air-driven fluid pump. The results were shown in Fig. 6. It was found that the retention of the RY84 was practically not changed up to 3 mL min^{−1} of flow rate. However, at flow rates higher

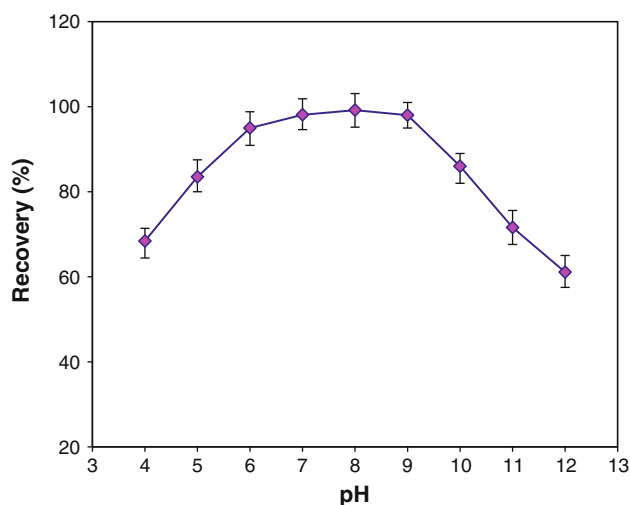


Fig. 5 Effect of pH on the retention of RY84 on Zn–Al(NO₃[−]) LDH nano-sorbent

than 3 mL min^{-1} the retention efficiency of RY84 reduced. Hence, a flow rate of 3 mL min^{-1} was employed in this work.

Optimization of elution conditions

Some experiments were carried out to select a proper eluting reagent for elution of the retained RY84 from the Zn–Al(NO_3^-) LDH nano-sorbent. For this purpose, various eluent such as NaOH, NaCl and Na_2CO_3 were tested. The results showed that the best recovery was achieved when NaOH was used as eluent. The concentration, volume and flow rate of the NaOH solution were also optimized. For this reason, various concentrations ($0.25\text{--}4 \text{ mol L}^{-1}$) of NaOH were studied for the elution of retained RY84 from the column. Based on the obtained results, 3 mol L^{-1} NaOH was sufficient for complete elution of the retained RY84 on the nano-sorbent. By keeping the eluent concentration at 3 mol L^{-1} , the effect of eluent volume ($0.5\text{--}4 \text{ mL}$) on the recovery was also investigated. The recovery value of the RY84 increased by increasing the NaOH volume up to 2.5 mL and remained constant afterward (Fig. 7). Therefore, optimum volume of the eluent and its flow rate was chosen as 2.5 mL and 1 mL min^{-1} , respectively.

Effect of the amount of zinc–aluminum layered double hydroxide nano-sorbent

The amount of SPE material is another important factor on the column studies for the quantitative recoveries of analytes. The effect of the amount of Zn–Al(NO_3^-) LDH on the retention of RY84 at pH 8 was examined in the range of

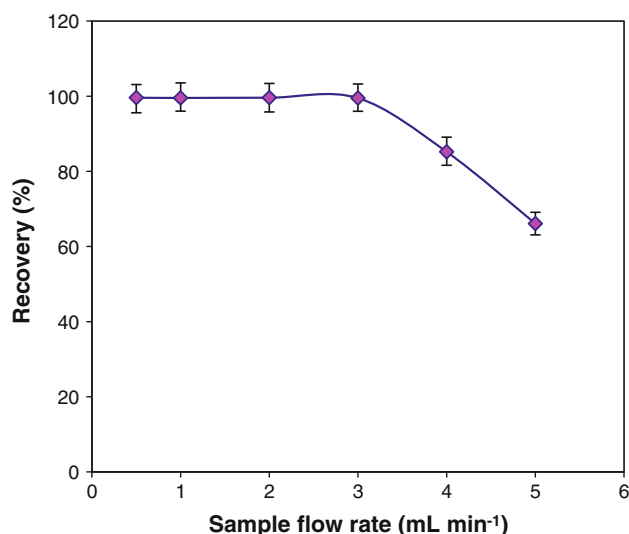


Fig. 6 Effect of sample loading flow rate on the retention of RY84 on Zn–Al(NO_3^-) LDH nano-sorbent

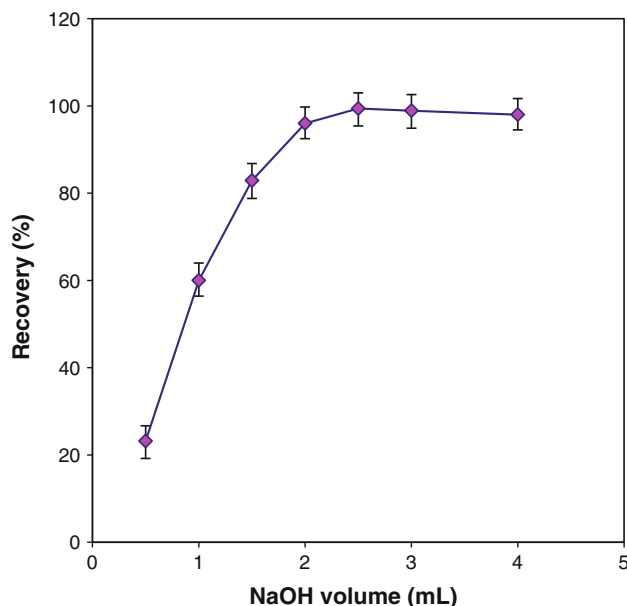


Fig. 7 Effect of eluent volume on the recovery of RY84 from Zn–Al(NO_3^-) LDH nano-sorbent

$50\text{--}400 \text{ mg}$. The results demonstrated that, quantitative recoveries ($>95 \%$) of the RY84 were observed when the amount of the LDH was higher than 150 mg . Therefore, in the presented procedure, 300 mg of Zn–Al(NO_3^-) LDH is recommended.

Effect of sample volume

An important parameter to control SPE of real samples is the sample volume. The effect of sample solution volume on the RY84 retention was investigated by passing $10\text{--}250 \text{ mL}$ sample solutions containing $120 \mu\text{g}$ of RY84 at a flow rate of 3 mL min^{-1} , according to the recommended procedure. As shown in Fig. 8, the recovery value of RY84 was found to be quantitative when sample volume was chosen between the ranges of $10\text{--}150 \text{ mL}$. Above 150 mL , the recovery decreased for the analyte. So, 150 mL was chosen as optimum sample volume.

Retention capacity

The retention capacity of the Zn–Al(NO_3^-) LDH nano-sorbent was obtained by the batch technique. For this purpose, 200 mg of the sorbent was added to 50.0 mL of solution containing 200 mg L^{-1} of RY84 and stirred for 60 min with magnetic stirrer and filtered through a filter paper. Retained RY84 onto LDH nano-particles were eluted with 5 mL of 3.0 mol L^{-1} NaOH prior to the determination. As a result, capacity of the Zn–Al(NO_3^-) LDH for RY84 was found to be 13.75 mg g^{-1} .

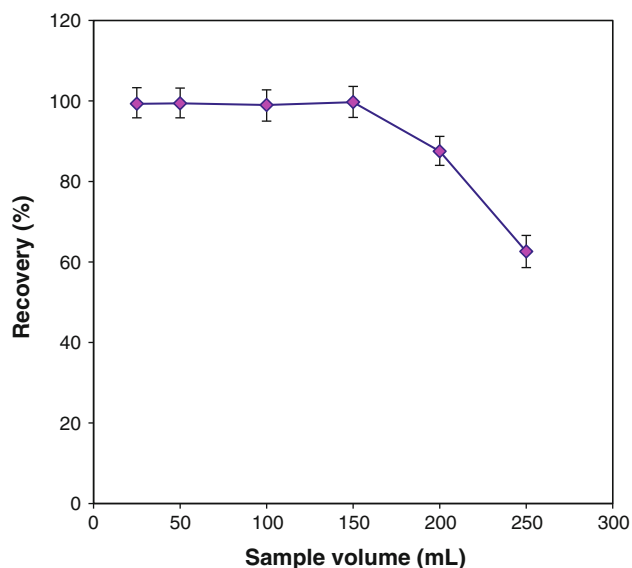


Fig. 8 Effect of sample volume on the removal of RY84 by Zn–Al(NO₃)₂ LDH nano-sorbent

Reusability of the zinc–aluminum layered double hydroxide nano-sorbent

The potential regeneration and stability of the column were also investigated. The column could be reused after regenerating with 3 mL of 3 mol L⁻¹ NaOH and 5 mL deionized water, respectively. Moreover, after at least 250 times of recycling, there is no obvious decrease or increase for the recovery of the analyte. The results indicate that the Zn–Al(NO₃)₂ LDH nano-sorbent is stable as well as no carryover of analyte during SPE procedure, showing good reusability.

Study of interferences

The effect of some co-existing ions on the extraction and determination of the RY84 was investigated. In this experiment, the solutions of RY84 containing the added interfering ions were treated according to the procedure of column experiments. The content of target analyte in the effluent was determined to calculate the recovery of the studied elements. The tolerance limits of the co-existing ions, defined as the maximum concentration of the foreign ion causing a change in the analytical signal no higher than

Table 2 Tolerance limits of interfering ions in the separation and determination of 0.8 μg mL⁻¹ of RY84

Coexisting ions	Interference to analyte ratio	Change in signal (%)
Br ⁻ , I ⁻ , K ⁺ , Na ⁺ , NO ₃ ⁻ , Ca ²⁺ , Mg ²⁺	1,000:1	-2.0, -1.0, +2.0, -2.0, +2.3, -2.0, -3.0
F ⁻ , IO ₃ ⁻ , Cl ⁻ , Fe ³⁺	800:1	-1.0, -2.0, +4.0, +3.0
H ₂ PO ₄ ⁻ , HCO ₃ ⁻	600:1	-2.0, -4.5
Al ³⁺ , CH ₃ COO ⁻ , CO ₃ ²⁻ , H ₂ PO ₄ ²⁻ , Zn ²⁺	400:1	+4.0, -2.0, +2.3, -2.0, +3.0

Table 3 Optimum SPE conditions and analytical parameters of the presented method for RY84 separation and determination

Parameters	Unit	
<i>SPE conditions</i>		
Sample consumption	(mL)	150
Working pH	–	8
Amount of Zn–Al(NO ₃) ₂ LDH	(mg)	300
Eluent concentration	(mol L ⁻¹)	3
Eluent volume	(mL)	2.5
Sample loading flow rate	(mL min ⁻¹)	3
Elution flow rate	(mL min ⁻¹)	1
<i>Analytical parameters</i>		
Linear range	(μg mL ⁻¹)	0.15 – 1.5
Intercept	–	0.034
Slope	–	1.033
Correlation coefficient	–	0.9982
Limit of detection (LOD) ^a	(μg mL ⁻¹)	0.04
Relative standard deviation (RSD) (n = 6)	(%)	1.8 (0.8) ^b

^a Calculated as three times the standard deviation of the blank signal divided by the calibration curve slope

^b Value in parentheses is the RY84 concentration (μg mL⁻¹) for which the RSD was obtained

±5 % are given in Table 2. It can be seen that most of examined cations and anions did not interfere with the extraction and determination. Therefore, the presented method is selective for the removal of RY84 dye from aqueous solutions.

Analytical performance

Under the experimental conditions, a series of experiments were designed for obtaining linear range, precision and detection limit. Table 3 shows the optimum conditions and analytical characteristics of the method. The calibration graph was linear between 0.15 and 1.5 μg mL⁻¹, with a correlation coefficient of 0.9982. The regression equation was $A = 1.033C + 0.034$, where C is the concentration of RY84 in μg mL⁻¹. The limit of detection, calculated as three times the standard deviation of the blank signal divided by the calibration curve slope, was 0.04 μg mL⁻¹. The relative standard deviation resulting from the analysis

Table 4 Determination of RY84 in wastewater samples (results of recoveries of spiked samples analysis)

Samples	Added RY84 ($\mu\text{g mL}^{-1}$)	Found RY84 ^a ($\mu\text{g mL}^{-1}$)	Recovery (%) ^b
Wastewater 1 ^c	–	0.180 \pm 0.002	–
	0.100	0.278 \pm 0.003	98.0
	0.200	0.374 \pm 0.001	97.0
	0.400	0.590 \pm 0.001	102.5
Wastewater 2 ^d	–	0.152 \pm 0.002	–
	0.100	0.252 \pm 0.004	100.0
	0.200	0.350 \pm 0.001	99.0
	0.400	0.550 \pm 0.003	99.5
Wastewater 3 ^e	–	0.205 \pm 0.002	–
	0.100	0.303 \pm 0.005	98.0
	0.200	0.397 \pm 0.003	96.0
	0.400	0.587 \pm 0.001	95.5
Wastewater 4 ^f	–	Not detected	–
	0.200	0.198 \pm 0.002	99.0
	0.400	0.394 \pm 0.001	98.5

^a Mean of three experiments \pm standard deviation

^b Recovery (%) = [(Found – Base)/Added] \times 100. “Base” and “Found” refer to the amount of RY84 in samples before and after spiking, respectively

^c Collected from wastewater effluent of Nahid Textile Factory, Esfahan, Iran

^d Collected from wastewater effluent of Behtab Textile Factory, Shahreza, Iran

^e Collected from wastewater effluent of Hadaf Textile Factory, Esfahan, Iran

^f Collected from wastewater effluent of Khoy Textile Factory, Khoy, Iran

of six replicates of 150 mL solution containing 0.8 $\mu\text{g mL}^{-1}$ RY84 was 1.8 %. As the amount of RY84 in the sample solution was measured after a final volume of 2.5 mL, the solution was concentrated by a factor of 60.

Analysis of real samples

To explore the feasibility of the presented SPE procedure, the methodology was applied to separation and determination of RY84 in several textile wastewater samples. In order to verify the accuracy of the established procedure, recovery experiments were carried out by spiking the samples with different amounts of RY84 before any pre-treatment. Table 4 shows the obtained results. As can be seen, recoveries between 95.5 and 102.5 % were obtained, which confirm the accuracy of the presented method.

Conclusions

In this research, a nano-sorbent from layered double hydroxides group has been reported. LDHs can be regarded as a class of materials that are simple to synthesize in the laboratory. It was found that the nanometer-sized Zn–Al(NO₃[–]) LDH is stable and has a great potential as a sorbent for the removal of dyes from aqueous solutions.

Also, Zn–Al(NO₃[–]) LDH has a high retention capacity regarding RY84 dye, and the retained analyte can be easily stripped with NaOH. On the other hand, the coupling of Zn–Al(NO₃[–]) LDH nano-sorbent for SPE procedure with spectrophotometric detection exhibits a sensitive, reproducible, simple, low cost technique that can be used for the separation and determination of RY84 dye in textile wastewater effluents.

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