Journal of Molecular Liquids 249 (2018) 254–264

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Starch-NiFe-layered double hydroxide composites: Efficient removal of methyl orange from aqueous phase

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ARTICLE INFO

Article history:
Received 23 August 2017
Received in revised form 25 October 2017
Accepted 2 November 2017
Available online 06 November 2017

Keywords:
Methyl orange
Starch-layered double hydroxides
Adsorption
Kinetic
Thermodynamics

ABSTRACT

Starch-NiFe-layered double hydroxide (S/NiFe-LDH) composite was prepared via co-precipitation method and employed as an adsorbent for the removal of anionic dye methyl orange (MO) from aqueous solution. Two hybrids with different ratio of starch and NiFe-LDH were prepared i.e. S/NiFe-LDH (1:1) and S/NiFe-LDH (2:1) and their adsorption performance was compared with NiFe-LDH. The synthesized nanocomposites were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), X-ray diffraction (XRD), and thermogravimetric analysis (TGA). The effects of influential adsorption parameters such as pH, initial MO concentration contact time and adsorbent dosage on the removal of MO were studied. The starch-NiFe-LDH composite was efficient in removing MO from water and maximum removal of 99 and 90% was observed at pH 3 by S/NiFe-LDH (1:1), S/NiFe-LDH (2:1), respectively. The maximum adsorption capacities of NiFe-LDH, S/NiFe-LDH (2:1) and S/NiFe-LDH (1:1), calculated from Langmuir isotherm, were 246.91 mg/g, 358.42 mg/g, 387.59 mg/g respectively. The adsorption kinetics of MO on the surface of S/NiFe-LDH composites was best fitted by pseudo-second-order model. Starch-NiFe-LDH was easily regenerated with aqueous solution of NaOH with a minor loss in adsorption capacity up to four cycles.

1. Introduction

Presence of numerous hazardous dyes and heavy metals in wastewater released from various industries is one of the serious global environmental concern [1–3]. According to recent reports, more than one million dyes are commercially available with annual production of over 7×10^5 tons [4]. The textile industry worldwide consumes approximately 1×10^4 tons of dyes annually and discharges nearly 100 tons/year of dyes into wastewater [1,4,5]. These dyes are highly toxic, carcinogenic and mutagenic and caused serious consequences to human health and marine system. The removal of these dyes from industrial waste streams is extremely desirable in order to meet regulatory obligations for recycle or discharge [5–9]. Methyl orange (MO) is highly carcinogenic and mutagenic in nature and excessively utilizes in dyeing industries [10–14]. Therefore, it is extremely important to get rid of this dye from waste stream before its discharge to aqueous bodies.

Various effluent treatment techniques such as adsorption [1,15–18], membrane filtration [2], chemical oxidation [19], ozonation [20], biological treatment [21], biosorption [22], ion exchange [4,23], coagulation and flocculation [4,14,24] have been reported widely to remove dyes and other pollutants from aqueous medium. Among all treatment techniques, adsorption is widely adopted due to its high removal efficiency, low process cost and ease of operation. Selection of appropriate adsorbent is critical for obtaining the maximum adsorption performance. Scientists, engineers and researcher are in quest of the low toxic adsorbents that exhibit higher removal efficiency, greater sustainability and wide range of effluents capturing ability. Various materials have been investigated for the adsorptive removal of dyes from wastewater such as carbon nanotubes [25], red mud [26], chitosan [27], fly ash [28], activated sludge biomass [29], activated carbon [30], rice husk [31], peat [32], zeolite [33], ferrite nanoparticles [34–36] and corn stalk [37].

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https://doi.org/10.1016/j.molliq.2017.11.022
0167-7322/

However, it is still indispensable to explore novel adsorbents with high adsorption capabilities for different pollutants. Layered double hydroxides (LDHs), also known as hydrotalcite clays or anionic clay have been attracted significant attention in recent years due to its application in various fields such as water treatment [38,39], catalysis [40], polymer nanocomposites [41] and biotechnology [42].

LDHs can be expressed by the general formula: $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-})_{x/m}\cdot mH_2O$, where M^{2+} and M^{3+} are divalent and trivalent metal cations, respectively, x is the molar ratio of trivalent cations ($0.2 < x < 0.33$), while A^{n-} is the interlayer anion with charge [2,6,7,13]. LDHs have been considered excellent adsorbent materials for wastewater treatment owing to their high surface area, layered structure and interlayer ion exchange [6,13]. Recently, LDH containing hybrids i.e. coupling of LDHs with different anions, carbon-based materials, and polymers, showed tremendous adsorption behavior for various toxic pollutants and attracted considerable attention for waste water treatment [38]. Yang et al. reported effective removal of MO from aqueous solution with magnetic GO/NiAl hybrid [43]. Ruan et al. studied the adsorption performance of reduced GO/NiCr towards MO and concluded promising adsorbent for the remediation of anionic dyes in wastewaters [44]. Other LDHs containing hybrids such as Fe_3O_4/ZnCr [45], glycerol-modified/MgAl-LDH [1], CNT/MgAlO [46] also demonstrated highly effective and promising performance for the adsorption of various dyes from aqueous phase.

Starch, a low cost second abundant polysaccharide has been extensively used in various fields such as packaging, drug delivery, food additives and water purification [47]. Due to its non-toxicity, biodegradable nature, and cost effectiveness, a number of starch based composites have been prepared and showed remarkable adsorption tendency for the removal of heavy metal and dyes [48–53].

The aim of this study is to produce a novel sustainable, environmental friendly and effective adsorbent for water treatment by coupling the unique properties of low cost starch with layered double hydroxides. In this work, starch-NiFe-LDH (S/NiFe-LDH) composites were prepared via co-precipitation method and applied for the removal of MO from aqueous solution. The composites were characterized by SEM, XRD, FTIR and TGA. Batch adsorption experiments were performed to study the effect of pH, adsorbent dosage, contact time, initial MO concentration and temperature on the removal of MO from water. The adsorption equilibrium and kinetics were analyzed using isotherm and kinetics models.

2. Materials and methods

2.1. Materials

Corn starch containing 27% amylose was purchased from Arasco corn products, Dammam, Saudi Arabia. Iron(III) nitrate nonahydrate [$Fe(NO_3)_3\cdot 9H_2O$], and nickel(II) nitrate hexahydrate [$Ni(NO_3)_2\cdot 6H_2O$] were purchased from Sigma Aldrich Co. (USA). All solvents and materials were analytical grade, and used without any purification. The characteristics of the MO dye are listed in Table 1. The stock solution of 1000 mg/L concentration of MO dye was prepared and diluted to the requisite concentrations by using de-ionized water.

2.2. Preparation of starch-NiFe (S/NiFe-LDH) composites

The starch-NiFe-LDH composites were prepared via co-precipitation method. Initially a known amount of 3:1 mole ratio of nickel and iron salts (M^{2+}:M^{3+}) were dissolved in 50 mL of deionized (DI) water in a reactor equipped with a magnetic stirrer. Simultaneously, certain amount of starch corresponded to starch and NiFe-LDH ratio (Table 2) was also dissolved in 100 mL deionized water, sonicated for 5 min and transferred to the reaction vessel. The solution was stirred vigorously for 15 min at 90 °C. Subsequently, the pH of the solution was adjusted to 10 ± 0.5 using 1 M NaOH solution. After maintaining the desired pH, the reactor was subjected to refluxing at 90 °C for 24 h. The resultant suspension was centrifuged and washed with DI water, followed by ethanol washing for the removal of impurities. The dense slurry was then dried at 40 °C in oven for 48 h. The S/NiFe-LDH composites were then stored in a desiccator for further use. The actual compositions of S/NiFe-LDH composites are listed in Table 2.

2.3. Characterization of NiFe-LDH and S/NiFe-LDH composites

The synthesized NiFe-LDH and S/NiFe-LDH composites were characterized by Fourier transform-IR (FTIR, Nicolet 6700, resolution 4 cm^{-1}), X-ray diffraction (XRD, D8 advance X-ray instrument, wavelength = 0.1542 nm, and $2\theta = 10°$ to 80°), scanning electron microscopy (SEM, SM-6460LV (Jeol)) and thermal gravimetric analysis (TGA Q-600 TA instrument at heating rate 10 °C/min).

2.4. MO adsorption studies

Batch adsorption experiments were performed to explore the effect of key influential adsorption parameters such as initial dye concentration, pH, adsorbent dosage, and contact time through equilibrium and kinetics studies. Nearly 0.01 g of each adsorbent was agitated for 10–360 min at 275 rpm in 30 mL of MO solution (20 − 200) mg/L using 50 mL plastic tubes at temperature (25–45 °C). The appropriate pH of the mixture was adjusted using 0.1 mol/L HNO_3 and NaOH solutions. After agitation, the mixture was centrifuged at 2000 rpm for 5 min to separate the spent adsorbent from the residual dye. The final concentration of the residual dye was calculated by Hach Lange spectrophotometer set at a maximum wavelength of 464 nm.

The amount of the dye adsorbed on the adsorbent q_e (mg/g) and percentage removal efficiency were estimated according to Eqs. (1) and (2), respectively.

$$\text{Adsorption capacity} = q_e = \frac{(C_0 - C_e)\,V}{W} \quad (1)$$

$$\text{Percentage removal} = \frac{(C_0 - C_e)}{C_e} \times 100 \quad (2)$$

where, C_0 and C_e are the initial and equilibrium concentration (mg/L) of MO in solution, respectively, q_e (mg/g) is the equilibrium adsorption capacity, W (g) is the weight of the adsorbent, and V (L) is the volume of the solution.

Table 1
Characteristics of methyl orange.

Chemical formula	Color index/type	λ_{max}	Molecular weight
$C_{14}H_{14}N_3NaO_3S$	13,025/anionic dye	Four hundred and sixty four nanometre	327.33

Table 2
Composition of S/NiFe-LDH composites.

Sample name	Starch (g)	Ni (g)	Fe (g)
NiFe-LDH	0	1.25	0.75
S/NiFe-LDH (1:1)	2	1.25	0.75
S/NiFe-LDH (2:1)	4	1.25	0.75