Journal of Colloid and Interface Science 458 (2015) 315–322

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

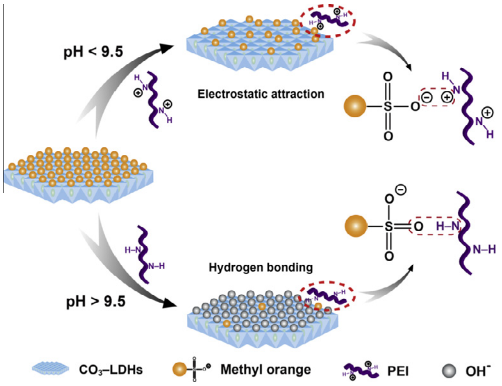
journal homepage: www.elsevier.com/locate/jcis

Polyethyleneimine as a novel desorbent for anionic organic dyes on layered double hydroxide surface

Siming Wang, Zenghe Li, Chao Lu *

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 30 June 2015
Revised 23 July 2015
Accepted 23 July 2015
Available online 26 July 2015

Keywords:
Layered double hydroxides
Polyethyleneimine
Desorption
Anionic dye
Electrostatic attraction
Hydrogen bonding

ABSTRACT

Polyethyleneimine (PEI) is a positively charged polymer with hydrogen-bonding sites and hydrophobic chains. Therefore, it has been clearly established as an efficient adsorbent by means of these native properties in the literatures. However, there is apparently no good reason to disregard the use of PEI as a desired desorbent. Herein, using methyl orange as a model anionic dye, we investigated the desorption performances of PEI toward anionic dyes adsorbed on the surface of CO_3–layered double hydroxides (LDHs) in a wide range of pH values. The experiment results showed that the positively charged PEI had very strong desorption capacity for anionic dyes at low pH values (<9.5) through electrostatic attraction between PEI and methyl orange because of the high degree of protonation of PEI. At high pH values (>9.5), PEI existed as neutral molecule, it could desorb methyl orange *via* hydrogen bonding between the amino groups of it and sulfonate group of methyl orange; simultaneously, the anion-exchange process occurred between abundant hydroxyl anions and anionic methyl orange. The adsorption capacity of the used LDH adsorbent was about 80% after five cycles of adsorption–desorption–regeneration, which was much higher than that conducted by 0.1 M NaOH solution. These findings suggested that PEI could be regarded as a promising desorbent for enriching anionic dyes in wastewater and regenerating LDHs through surface adsorption–desorption cycles.

1. Introduction

Layered double hydroxides (LDHs), also known as hydrotalcite-like compound or anionic clay, are a class of two-dimensional structure materials with a general formula of $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}$

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* Corresponding author.
E-mail address: luchao@mail.buct.edu.cn (C. Lu).

http://dx.doi.org/10.1016/j.jcis.2015.07.056
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$(A^{n-})_{x/n} \cdot mH_2O$, where M^{2+} denotes divalent metal ion, M^{3+} represents trivalent metal ion, A^{n-} is the interlayer anion with valance n, and x is equal to the molar ratio of $M^{3+}/(M^{2+} + M^{3+})$ typically ranging from 0.18 to 0.33 [1–3]. The remarkable interlayer anion-exchange capacity, high positive charge, and large specific surface area allow LDHs to become effective adsorbents to capture a range of anionic dyes in aqueous solutions [4–7]. In comparison with other adsorbents, LDHs can be easily recycled by anion exchange, which is attracting current research interest [8,9]. However, considerable examples have been reported on adsorptive properties of LDHs toward anionic dyes, few studies have addressed desorption of anionic dyes [10]. Generally, NaCl–NaOH, Na_2CO_3, or high-press CO_2 is employed as efficient desorbents to remove adsorbed anions from LDH materials *via* anion exchange process [11–14]. However, these desorbents require to be in high concentrations (e.g., 20% NaOH) [11] and desorption efficiencies are unsatisfactory (about 50%) [12,13]. Therefore, it is extremely necessary to investigate a new strategy to improve the desorption efficiency of anionic dyes from LDHs.

Polyethyleneimine (PEI) is a cationic water-soluble polymer with a large number of primary, secondary and tertiary amino groups (Fig. S1a) [15,16]. The protonation of amine groups on the macromolecular chains of PEI leads to its positive charges, facilitating the electrostatic attraction toward negatively charged compounds [17]. On the other hand, a great number of amino groups could generate very strong interactions between PEI and some organic compounds *via* hydrogen bonding [18]. Notably, the hydrophobic vinyl of PEI can interact with hydrophobic chains of some compounds through hydrophobic interaction [19]. Therefore, PEI with the three predominant features exhibits strong adsorption capacity for a series of substances [20–23]. For example, PEI was grafted onto the surface of nanoparticles to improve the adsorption capacity of nanoparticles toward anionic contaminants through electrostatic attraction [24]. The PEI/SiO_2 composite material was successfully fabricated to adsorb 2,4,6-trinitrotoluene through hydrogen bonding between PEI and 2,4,6-trinitrotoluene [25]. Although there are many cases about the efficient adsorption capacity of PEI [20–23], to the best of our knowledge, no studies have investigated the use of PEI as a desired desorbent for the removal of adsorbed compounds from materials. There is apparently no good reason to disregard this promising desorbent.

In this work, the efficient desorption capacity of PEI toward anionic dyes adsorbed on the surface of CO_3–LDHs was evaluated by using methyl orange (Fig. S1b) as a model anionic dye. Interestingly, it was observed that the introduction of PEI in the methyl orange-adsorbed LDHs could easily desorb methyl orange from LDHs in a wide range of pH values. The regeneration rate of the used LDH adsorbent was about 80% after five cycles of adsorption–desorption–regeneration. The mechanism studies demonstrated that the desorption of methyl orange at low pH values was ascribed to electrostatic attraction between protonated PEI and negatively charged methyl orange. While, at high pH values, it was attributed to the cooperative contributions of hydrogen bonding between the sulfonate group of methyl orange and amino groups of PEI, as well as anion-exchange between abundant hydroxyl anions and anionic methyl orange.

2. Experimental

2.1. Materials

All reagents were of analytical grade obtained from commercial sources and used without further purification. Analytical grade chemicals, including $Al(NO_3)_3 \cdot 9H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, NaOH, Na_2CO_3, HCl, and methyl orange ($C_{14}H_{14}N_3O_3S \cdot Na$, >80.0%) were purchased from Beijing Chemical Reagent Company (Beijing, China). Branched PEI (M_w = 10,000, 99%) was purchased from Alfa Aesar, Great Britain. All solutions were prepared with deionized water (Milli Q, Millipore, Barnstead, CA, U.S.A.).

2.2. Apparatus

The X-ray diffraction (XRD) measurements were performed on a Bruker (Germany) D8 ADVANCE X-ray diffractometer equipped with graphite-monochromatized Cu Kα radiation ($\lambda = 1.5406$ Å). The 2θ angle of the diffractometer was stepped from 5° to 70° at a scan rate of 10°/min. The Fourier-transform infrared (FTIR) spectra (resolution: 2.0 cm^{-1}, number of scan: 32) were obtained with a Nicolet 6700 FTIR spectrometer (Thermo, U.S.A.) using the KBr disk technique. Tecnai G220 (FEI, Hong Kong) transmission electron microscopy (TEM) at an accelerating voltage of 200 kV was used for observing the particle sizes and external morphology of the samples. The scanning electron microscopy (SEM) images were obtained using S-4700 field-emission SEM. N_2 adsorption–desorption isotherm was measured at 77 K using ASAP 2020 nitrogen adsorption apparatus (Micromeritics Ins. Corp., USA). The pore-size distribution of sample was calculated according to desorption branch using the Barrett–Joyner–Halenda (BJH) method. And specific surface area was calculated from the linear part of the BET plot using the Brunauer–Emmett–Teller (BET) equation. The zeta potential measurements of the samples were determined on a Zetasizer 3000HS nano-granularity analyzer from Malvern Instruments (UK). A Shimadzu UV-2401 spectrophotometer was used to record the UV–vis spectra of various samples. The pH values were detected using a Five Easy pH meter (Mettler Toledo Instrument Company, Shanghai, China). The centrifugation was operated on a TGL-16B centrifugal machine (Shanghai Anting Scientific Instrument Factory, Shanghai, China) or a Z-326K centrifugal machine (Hermle Labortechnik GmbH, Germany).

2.3. Synthesis of Mg–Al–CO_3 LDHs

In comparison to traditional coprecipitation method, the structure of LDHs under hydrothermal method was more stable, facilitating the consecutive adsorption–desorption cycles of LDHs [26,27]. Therefore, the Mg–Al–CO_3 LDHs were synthesized by a hydrothermal route in this work. Generally, 0.02 mol of $Mg(NO_3)_2 \cdot 6H_2O$ and 0.01 mol of $Al(NO_3)_3 \cdot 9H_2O$ were dissolved completely in 30 mL of deionized water to obtain solution A. Solution B was prepared by dissolving 0.06 mol NaOH and 0.01 mol Na_2CO_3 in 30 mL of deionized water. Solution A and solution B were mixed quickly under magnetic stirring. Then a certain amount of 1.0 M NaOH solution was added to the above mixture to adjust the pH value to 11.0 and the mixture solution was continuously stirred for 0.5 h. Afterward, this mixture solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and kept for 20 h at 200 °C. Finally, after cooling to the ambient temperature naturally, the obtained white precipitate was centrifuged, washed thoroughly with deionized water three times, and finally dried in a vacuum oven for 24 h at 60 °C.

2.4. Adsorption experiments

For the adsorption isothermal experiments, a series of 20 mL methyl orange solutions from 20 to 100 mg/L were prepared in advance. The pH values of all the solutions were adjusted with 1.0 M HCl to 4.0. Then 8.0 mg CO_3–LDHs were added to every methyl orange solution. Particles after equilibrium were separated by centrifugation (10,000 rpm/min, 5 min), the residual methyl orange concentrations in the sample solutions were determined by the UV–vis spectrophotometer at 464 nm. And the remainder