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Reactive orange 5 removal from aqueous solution using hydroxyl ammonium ionic liquids/layered double hydroxides intercalation composites

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HIGHLIGHTS

- The intercalation of the anion of ILs into the interlayer of LDHs was confirmed.
- The maximum adsorption capability of ILs/LDHs reached up to 300.9 mg/g.
- The adsorption kinetics, isotherm, thermodynamic and mechanisms were discussed.
- The ILs/LDHs might be used as an efficient adsorbent for dye waste water.

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ABSTRACT

A series of hydroxyl ammonium ionic liquids/layered double hydroxides intercalation composites (ILs/LDHs) were synthesized and adopted to study the adsorption process of anionic dye reactive orange 5 from aqueous solutions. The ILs/LDHs and LDHs were characterized by infrared spectroscopy (IR), X-ray diffractometry (XRD), thermogravimetric analysis (TG), total organic carbon (TOC) analyzer and BET surface area measurement. The successful intercalation of the anion of ILs (2-hydroxyethylammonium acetate) into the interlayer space of LDHs was confirmed. The effects of contact time, temperature, adsorbent dosage and solution pH on the adsorption experiments were investigated. The experimental results showed that the maximum adsorption capability of ILs/LDHs reached up to 300.9 mg/g, which was obviously higher than that of LDHs. The adsorption isotherms were well described by Freundlich model in the presence of the LDHs and ILs/LDHs. The adsorption kinetics followed the pseudo-second order kinetic model. The negative value of ΔG^0 and the positive value of ΔH^0 indicated spontaneous and endothermic nature of reactive orange 5 adsorption. For ILs/LDHs(b), desorption percentages were 57.91%, 46.67%, and 37.34% in each cycle, respectively. This innovative approach, using ILs/LDHs, was more efficient and could be envisaged as a promising process for reducing the pollution of the textiles manufacturing.

1. Introduction

Textile industry is one of the fast growing industries and significantly contributes to the economic growth in china. However, the textile dyeing industry consumes large quantities of water and produces large volumes of wastewater. The major pollutant of textile wastewater comes from the dyes which are not dyed or washed down after dyeing [1]. From the point of view of production practice, ten to twenty percent of dyes are poured into the dyeing–printing wastewater during the dyeing and printing process [2]. Unfortunately, on account of the complex and stable chemical structure, most of these dyes are toxic and poor biodegradation, and dyeing wastewater discharge is able to reduce aquatic diversity by blocking the passage of sunlight through the water and affect human health.

At present, many methods, such as coagulation or flocculation, chemical oxidation, biological treatment, membrane filtration, photodegradation, adsorption and etc [3–8], have been studied in order to remove the dyes from the textile wastewater. Among the above treatment techniques, the adsorption method is regarded as one of the most economical and effective way to deal with the dyed wastewater [9,10]. For example, activated carbon has been used as the adsorbent in some industrial water treatment devices to remove the dyes from the wastewater. In recent years, a lot of attention has been focused on preparing the adsorption

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material with low-cost and high adsorption capacity, like clay minerals, polymers, nano materials, silica and so forth [11–14].

Layered double hydroxides (LDHs), known as the anionic clay, have become an important kind of adsorbents for treating the wastewater owing to its efficient adsorption and reusability. In brief, hydrotalcites are referred to as layered double hydroxide with the general formula $[M_{1-x}{}^{II}M_x{}^{III}(OH)_2]^{x+}[A^{n-}]_{x/n}{\cdot}mH_2O$, where M^{II} and M^{III} stand for a divalent and a trivalent cation [15,16], respectively, A^{n-} is the interlayer anion, such as CO_3^{2-}, Cl^-, NO_3^- and etc, which is located in the interlayer and the lamellar surface. Due to their anionic exchange capacity, LDHs are suitable for sorption of anionic species [17]. Moreover, the adsorption capacity of LDH is largely influenced by the anion.

Nowadays, LDHs have been modified in various forms in order to improve their adsorption capacity [18–20], such as calcination and the organic modification. Zaghouane-Boudiaf et al. [21] investigated the adsorption of methyl orange on calcined MgNiAl LDHs and their precursor and found a much higher adsorption on calcined MgNiAl LDHs than their precursor without heat treatment. Miranda et al. [22] used dodecylsulfate (DS) and dodecylbenzenesulfonate (DSB) anionic surfactants to modify hydrotalcite-iron oxide magnetic so as to improve the adsorption efficiency of the LDHs, and the removal percentages of methylene blue (MB) dye had increased by 81% and 73%, respectively. Liu et al. [23] even used LDHs-bacteria aggregates to enhance the decolourisation of methylene blue. In a word, utilization of LDHs and derivations could bring great economical and environmental benefits to dyeing wastewater industries.

In recent years, room temperature ionic liquids (ILs) have become the research emphasis in consequence of their unique properties, such as extremely low vapor pressures, fine stability and outstanding solubility. Accordingly, ILs can certainly be used as dye extractant to achromatize aqueous solution [24,25]. However, such kind of green material is difficult to have a role in the dyes wastewater treatment because of high price, low liquidity and unsatisfactory mass transfer efficiency. Facing these problems, immobilization of ILs on solid supports may improve their applicability in industrial processes. Gao et al. [26] had synthesized a functional ionic liquid cross-linked polymer to adsorb anionic azo dyes, the experimental results showed that the performance of it is superior to other adsorbents and adsorption capacity could reach 547–925 mg/g for different anionic azo dyes. Ghaedi et al. [27] and Absalan et al. [28] had immobilized ILs on inorganic materials to improve the adsorption properties of these materials.

As mentioned above, Both LDHs and immobilized ILs are promising class of sorbents. However, to the best of our knowledge, the combination of LDHs and ILs has not been reported in literature. Therefore, the objectives of our work are to prepare a series of hydroxyl ammonium ionic liquids/layered double hydroxides composites (ILs/LDHs), which used as adsorbent for the removal of anionic dye reactive orange 5 from aqueous solution. The effects of various factors such as solution pH, and adsorbent dosage on adsorption have been investigated. Kinetic and isotherm models have also been discussed. The experimental results show that the adsorption capacity and performance of LDHs have improved significantly after inserting the ILs in their interlamination. This study can provide a reference for the dyes wastewater treatment using inexpensive and easily-obtained the intercalation composites.

2. Experimental

2.1. Materials

Ethanolamine, 2-(2-aminoethoxy) ethanol, triethanolamine, formic acid, ethanoic acid, lactic acid, ethyl alcohol, aluminum nitrate nonahydrate, magnesium nitrate hexahydrate, sodium hydroxide and sodium carbonate were all AR grade and purchased from Sinopharm Chemical Reagent Co., Ltd. reactive orange 5 was purchased from Jiangsu Shenxin Dyestuff Chemicals Co., Ltd. All reagents were used without further purification.

2.2. Sample preparation

Hydroxyl ammonium ionic liquids were synthesized according to the procedures described in literature [29].

The co-precipitation method was adopted for the preparation of ILs/LDHs intercalation composites. The reaction was conducted in a 500 mL four neck round bottom flask with a magnetic stirrer, two dropping funnel and a reflux condenser. 20 mL ILs and 35 mL water were mixed up uniformly and put into the flask. The mixture was heated to 90 °C in a thermostat water bath. A solution was prepared by mixing $Mg(NO_3)_2{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ (Mg^{2+}/Al^{3+} molar ratio of 2 and Mg^{2+} concentration is 0.6 M) in 100 mL of deionized water. This solution and the aqueous solution of 0.8 M NaOH were simultaneously added dropwise into a flask under vigorous stirring. Meanwhile, the pH value of the mixed suspension liquid should be controlled at about 10 during the dropping process. Afterwards, the samples should be acutely stirred for 3 h at 90 °C and then aged at 100 °C for 24 h. The precipitate was separated by suction filtration, washed with deionized water and dried in an oven at 80 °C for 12 h.

2.3. Characterization of the prepared materials

X-ray diffraction (XRD) patterns of the samples were obtained by Bruker D8 Advance, using filtered CuKα radiation (λ = 0.154 nm). 2θ angle of the diffractometer was stepped from 3° to 80° at a scan rate of 10°/min. FT-IR spectra were recorded on a Tensor 27 IR spectrometer (Bruker, Germany) using KBr disc technique. Thermal decomposition of LDHs and ILs/LDHs were evaluated by thermogravimetric analysis (TG) carried out on Diamond TG/DTA instrument under nitrogen atmosphere at 10 °C/min from room temperature up to 700 °C. The proportion of ILs(b) containing in ILs/LDHs(b) composite was analyzed by total organic carbon (TOC) analyzer (VarioTOC, Elernentar, Germany) at 950 °C. The pore structures of the LDH and ILs/LDHs were analyzed by N_2 adsorption–desorption at 77 K on an Automatic specific surface and porosity analysis physical adsorption instrument (ASAP 2020-M, Micromeritics, USA).

2.4. Adsorption

2.4.1. Effect of initial pH

This effect was studied on suspensions of adsorption material in 180 mg L^{-1} of reactive orange 5 dye solutions (solid/solution ratio = 0.5 g L^{-1}). The initial pH (the values varied from 4 to 11) of dye solutions was adjusted with 0.1 M Na_2CO_3 and 0.1 M ethanoic acid solutions (used to adjust pH in dyeing and printing industry). The suspensions were stirred at 25 °C during equilibrium times and then centrifuged. The dye equilibrium concentration in the supernatants was measured by visible spectrophotometer on METASH (V-5600) UV–vis spectrophotometer at 478 nm.

2.4.2. Effect of LDHs and ILs/LDHs dose

The effect was studied on suspension of LDHs or ILs/LDHs (solid/solution ratio varied from 0.1 to 0.9 g L^{-1}) in 60 or 180 mg L^{-1} of reactive orange 5 dye solution at natural pH of the dye (6.48). The suspensions were stirred during equilibrium times and then centrifuged. The dye equilibrium concentration in the supernatants was determined as above.