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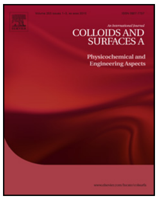

Adsorption capability for anionic dyes on 2-hydroxyethylammonium acetate-intercalated layered double hydroxide

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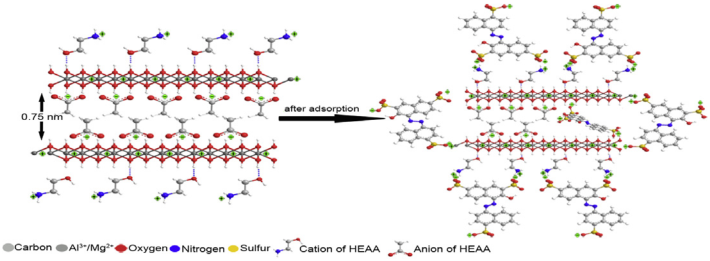
HIGHLIGHTS

- Proposed mechanism of interaction between hydrotalcite and ionic liquid.
- The electrostatic attraction plays main role in this adsorption.
- HEAA/LDHs effectively remove anionic dyes from aqueous solution.
- The maximum adsorption capability for acid red 27 was 313.6 mg/g.

GRAPHICAL ABSTRACT



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ABSTRACT

In the present study, organic dyes adsorption by MgAl-layered double hydroxides (LDHs) modified with 2-hydroxyethylammonium acetate (HEAA) ionic liquids were investigated. The characterization of XRD revealed that the anion of HEAA was inserted into the interlayer space of LDHs. Moreover, the intercalation composite (HEAA/LDHs) with an expanded layer distance was confirmed. HEAA/LDHs were further characterized by the SEM, FTIR, BET and zeta potential. The effects of contact time, types of dyes, adsorbent dosage and solution pH on the adsorption experiments were evaluated. The maximum of adsorption capability for acid red 27 was 313.6 mg/g. The adsorption process followed the pseudo-second-order kinetic equation. The equilibrium adsorption isotherm data were well fitted by the Langmuir model. The adsorption mechanisms proposed that electrostatic interaction and ion exchange played key roles in this adsorption process. Moreover, dyes could desorb easily from HEAA/LDHs by increasing pH values of the solution. The results suggested that modified LDHs could be employed as an efficient adsorbent material for the removal of anionic dyes from aqueous solutions.

1. Introduction

Organic dyes are one of the major classes of pollutants in wastewater. The dye molecules are commonly based on the complex aromatic structure which may lead to highly stable and resistant to biodegradation [1]. 10%–15% of the utilized dyes are discharged into the environment. The releases of dye wastewater into receiving stream not only affect the aesthetic nature but also are toxic to aquatic life and mutagenic and carcinogenic to human beings [2,3]. So the removal of dyes from wastewater before discharging into the natural water body is extremely important to environmental safety.

Different methods have been investigated for the removal of dyes from wastewater, including adsorption, coagulation, membrane filtration, oxidation, ozonation, etc [4–7]. In comparison with other techniques, adsorption is proved to be the more effective process due to its low cost, higher uptake capacity, greater selectivity, faster regeneration kinetics, less production of sludge and easy

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operation [8]. Various porous materials such as activated carbon, alumina and clay minerals are proposed for the removal of dyes from wastewater [9]. Moreover, absorbing materials with hierarchical nanostructure are also drawn increasing attention in recent years, such as MnO_2, iron hydroxide and iron oxides [10–12].

Layered double hydroxides (LDHs) are referred to as anionic clays 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, respectively, A^{n-} is the interlayer anion. LDHs are hydrotalcite-like materials, which have incorporated anions in the interlayer space due to partial substitution of trivalent for divalent cation. Incorporated anions can be exchanged by other anion [13–15]. Due to the exchangeability of the interlayer anion and the high charge density of the layers [16], LDHs are often used as adsorbing material for removing dyes from wastewater [17,18]. However, LDHs is not highly effective for adsorption in its virgin form because of its small layer distance and low density of active anchoring sites per unit surface area. The adsorption property of LDHs can be modified by the exchange of organic interlayered anion such as dodecylsulfate (DS) and dodecylbenzenesulfonate (DSB)[19,20]. Previous studies have suggested that the space between layers increases and alteration of interlayer superficial properties from hydrophilic to hydrophobic occur in the modified organo-LDHs.

In a previous work, we prepare a series of hydroxyl ammonium ionic liquids/layered double hydroxides intercalation composites (ILs/LDHs), the anion of ILs insert into the interlayer space of LDHs. As we have already known, there are two main drawbacks in the utilization of ILs, cost and viscosity. Immobilization of ILs can solve these problems, which have recently begun to draw attention [21]. ILs/LDHs were used as adsorbent for the removal of reactive orange 5 dyes from aqueous solution. The adsorption 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[22]. However, it is unclear how the dye is adsorbed in the intercalation composite, and the mechanism would be required further exploration.

In this study, 2-hydroxyethylammonium acetate/hydrotalcite (HEAA/LDHs) is synthesized, characterized and applied for removal of various types of dyes (anionic azo dyes, cationic dyes and nonionic dye). The effects of several factors, such as contact time, pH values and adsorbent dose are investigated. Thereafter, the equilibrium isotherm data are fitted with typical isotherms models. Kinetic models and the thermodynamics are used to evaluate the adsorption processes. In addition, both adsorption mechanism and intercalation behavior are explored at the microcosmic level.

2. Materials and methods

2.1. Reagents

Ethanolamine, ethanoic acid, ethyl alcohol, aluminum nitrate nonahydrate, magnesium nitrate hexahydrate, sodium hydroxide and sodium carbonate were AR grade and purchased from Sinopharm Chemical Reagent Co., Ltd. Acid red 27, direct red 23, disperse red 9 and methylene blue, used as model dyes, was obtained from Jiangsu Shenxin Dyestuff Chemicals Co., Ltd. All reagents were used without further purification.

2.2. Preparation of adsorbent

2-hydroxyethylammonium acetate (HEAA) ionic liquids were synthesized according to the procedures described in literature [23]. The HEAA/LDHs intercalation composites were synthesized by the co-precipitation method. 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 HEAA and 40 mL deionized H_2O were mixed in flask, and then an aqueous solution (62.5 mL) of $Mg(NO_3)_2\cdot 6H_2O$ and $Al(NO_3)_3\cdot 9H_2O$ (Mg/Al molar ratio equal to 2 and the total metal ion concentration of 0.9 M) and 200 mL of 0.8 M NaOH was added simultaneously and dropwise slowly under vigorous stirring. During the dropping process, the temperature was maintained at 90 °C and pH was kept at 10. The dropping process was maintained for 1.5 h. Afterwards, the suspension was stinging stirred at 90 °C for 3 h and then aged at 100 °C for 24 h. The precipitate was filtered, washed with deionized water repeatedly until the solution pH was neutral. The wet solid was dried at 80 °C.

2.3. Characterization

The X-ray diffraction (XRD) patterns of all samples were collected by Bruker D8 Advance (Cu Kα source, λ = 0.154 nm). FT-IR spectra were recorded on a Tensor 27 IR spectrometer (Bruker, Germany) using KBr disc technique. The morphology of the samples was observed on field emission scanning electron instruments (S-4800, Japan). The zeta potential of adsorbents was measured using Zetasizer Nano ZS90 instruments at pH values from 4 to 13. Specific surface area of the samples were measured by nitrogen adsorption at −196 °C using surface area and pore size analyzers (Autosorb-1-MP, Quantachrome), the samples were degassed at 200 °C for 2 h prior to measurements.

2.4. Study of dyes removal by HEAA/LDHs

Adsorption experiments were carried out by adding the adsorbents from 10 to 90 mg in a 100 mL dyes solution. The mixture was put into 250 mL conical flask in a thermostatic shaker. After sorption had occurred, the suspension was filtrated by using a 0.45 μm PES filter. The dye concentration in the solution was measured by UV–vis spectrophotometry (METASH, V-5600) at the maximum adsorption wavelength of each dye. The effects of adsorbents dose were evaluated on the adsorption capacity of dyes when varying from 0.1 to 0.9 g/L in 180 mg/L of dye solution. The effects of initial pH on adsorption were investigated at different initial pH; the initial pH was adjusted by addition of HCl or NaOH solution (0.01N).

Investigation of the kinetics of the adsorption process was performed at 25 °C. In the experiment, the solid/solution ratio was 0.5 g/L, the initial concentration of dye solution was 180 mg/L. Suspensions were stirred at different times (5 to 600 min) and then filtration. For studies of the sorption isotherms, the adsorbents (0.5 g/L) and dye solutions at different concentrations (10–210 mg/L) were stirred during equilibrium times at 25 °C. The adsorption thermodynamics experiment was performed at different temperatures.

The adsorption capacity q_e (mg of dye per g of sorbent) was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

Where C_0 is the initial dye concentration (mg/L) in the solution, C_e is the dye concentration (mg/L) at equilibrium. V is the initial volume (L) of the dye solution and m is the dry adsorbent dosage (g).

2.5. Desorption and recyclability experiments

In order to recover the adsorbent, after the adsorption of dye, the adsorbent was separated from the dye solution by centrifuging. And then the adsorbents were added to a solution (pH = 11.0, 25 °C, 500 mL) stirring for 4 h. The amount of desorbed dye was determined through the same method used in the adsorption stud-