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Research paper

Preparation, characterization and application on dye adsorption of a well-defined two-dimensional superparamagnetic clay/polyaniline/Fe_3O_4 nanocomposite

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ABSTRACT

Well-defined two-dimensional superparamagnetic clay/polyaniline/Fe_3O_4 nanocomposites were successfully prepared for dye adsorption based on montmorillonite and vermiculite via a one-pot method combining in-situ intercalation polymerization and coprecipitation technique. The results of XRD revealed that montmorillonite and vermiculite were well intercalated and even completely exfoliated by polyaniline and Fe_3O_4. Furthermore, the generated Fe_3O_4 nanoparticles with a diameter of about 10 nm and polyaniline were well confined to the surface of clay without the free aggregates. The as-prepared two-dimensional superparamagnetic nanocomposites could be served as a recycled adsorbent for the removal of dyes from aqueous solution by magnetic separation. The adsorption ratio toward 100 ppm of Brilliant green, Methylene blue, and Congo red reached 96.2%, 99.6% and 98.1%, respectively. In addition, the adsorption kinetics and the adsorption isotherm well fitted pseudo second-order kinetic model and Langmuir isotherm model, respectively. It suggested that the two-dimensional superparamagnetic nanocomposites exhibited excellent adsorption ratio to cationic dyes as well as anionic dyes.

1. Introduction

In the past centuries, natural clay minerals including one-dimensional palygorskite, sepiolite and two-dimensional montmorillonite (Mt), kaolinite, etc., were widely applied in various fields, and they were acknowledged to be exceptionally promising candidates as sustainable, and effective adsorbents for the removal of dyes, heavy metal ions and other pollutants due to their low cost, abundance in most continents of the world, high adsorption properties, and non-toxicity (Rafatullah et al., 2010; Wang and Wang, 2016). However, it was indispensable to enhance their adsorption property toward pollutants by surface modification due to the limited adsorption sites. Therefore, many physical treatments (lyophilisation, ultrasound, plasma, high-pressure homogenization, etc.) and chemical modifications (acid/alkali, surfactant, silane coupling agent, surface grafting of polymer, etc.) were developed for the surface modification of clay (Bergaya and Lagaly, 2001; Liu, 2007; de Paiva et al., 2008; Rodríguez-Cruz et al., 2008; Thanos et al., 2012; Mu and Wang, 2016). What is more, the modification of the two-dimensional clays using conductive polymer attracted increasingly attention in the field of water treatment owing to the high cation exchange capacity, the abundant active adsorption sites and organic functional groups (Fang et al., 2008).

Polyaniline (PANI), as one of the nitrogen-containing conductive polymers, was first described in the mid-19th century by Henry Letheby (Inzelt, 2008). Due to the advantages of easy synthesis, low-cost of the monomer, good environmental stability, and large amounts of amine and imine functional groups, PANI was incorporated into two-dimensional clays for the removal of pollutants from aqueous solution (Chen et al., 2013; de Barros et al., 2015). However, it was difficult to easily separate those adsorbents from the treated water via traditional centrifugation and filtration for recycling owing to the small size, as well as the time-consuming and uneconomic process. It was reported that the magnetic separation technology was a kind of efficient, rapid and inexpensive separation method (Lin et al., 2010; Zhu et al., 2010; Rossi et al., 2014). Thus it might be a feasible and efficient strategy for easy recycling by introducing magnetic nanoparticles based on the two-dimensional clay/PANI nanocomposites.

Reena et al. prepared the electromagnetic PANI-polyhydroxy iron-clay composites by oxidative radical emulsion polymerization of aniline in the presence of polyhydroxy iron cation intercalated clays (Reena et al., 2010). Bekri-Abbes and Srasra also proposed a facile strategy for fabrication of clay/PANI/iron nanocomposite via the one step solid state intercalation method (Bekri-Abbes and Srasra, 2015), in which

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both interlayer Fe(III) and atmospheric oxygen act as oxidant for aniline polymerization while Fe(III) and Fe(II) formed by the reduction of Fe(III) favors the formation of iron nanoparticles phase. In addition, we also developed a one-pot process for synthesis of multifunctional superparamagnetic palygorskite/Fe_3O_4/PANI for dye adsorption, the Au(III) enrichment and catalyst support using Fe(III) as the oxidant for aniline and the single iron source of Fe_3O_4 in the presence of palygorskite (Mu and Wang, 2015). It was worth noting that the modification mechanism of one-dimensional clays and two-dimensional clays was different. The modification of one-dimensional clays was only surface adsorption or encapsulation, while that of two-dimensional clays was not only surface adsorption or encapsulation, but also intercalation or even exfoliation. Thus this strategy possibly gave us an inspiration to prepare superparamagnetic two-dimensional clay/PANI/Fe_3O_4 nanocomposites.

In this study, the facile one-pot method was employed to prepare the well-defined two-dimensional superparamagnetic clay/PANI/Fe_3O_4 nanocomposites combining in-situ intercalation polymerization and coprecipitation technique based on Mt and vermiculite (VMT). In addition, the common dyes of Methylene blue (MB), Brilliant green (BG) and Congo red (CR) were selected as the targeted models to evaluate the adsorption properties of the as-prepared Mt/PANI/Fe_3O_4 nanocomposites, and the structural formula of three dyes was provided in Fig. S1. The incorporation of the active components and magnetic nanoparticles into two-dimensional clay layered structure was expected to achieve the efficient adsorption and easy separation of dyes and other pollutants from aqueous solution.

2. Experimental

2.1. Materials

Mt with cation exchange capacity of 90 meq/g was purchased from Southern Clay Products Inc. Unexpanded VMT was milled and passed through a 320-mesh screen provided by Gansu Xinyi Environmental Protection Chemical Co., Ltd., Gansu, China. BG was purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. MB and CR were purchased from Alfa Aesar Co. Ltd. $FeCl_3 \cdot 6H_2O$, aniline and other reagents were all of analytical reagent grade from Tianjin Chemical Co., China, and used without further purification. Ultrapure water (18.25 MΩ cm) was used throughout.

2.2. Preparation of two-dimensional superparamagnetic clay/PANI/Fe_3O_4 nanocomposites

In this study, the low-cost two-dimensional Mt was selected to fabricate the two-dimensional superparamagnetic Mt/PANI/Fe_3O_4 nanocomposites via one-pot method combining in-situ intercalation polymerization and coprecipitation technique, and this method was similar with that of our previous report (Mu and Wang, 2015). In a typical procedure, 0.5 g of Mt was added into 50 mL of water containing 0.5 mL of aniline, and the value of pH was adjusted to 4 using 1.0 M HCl. After being ultrasonically treated for 30 min, 3.552 g of $FeCl_3 \cdot 6H_2O$ was added into above solution, and the reaction was stirred for overnight at the room temperature. Then the reaction system was heated to 70 °C, and 10 mL of $NH_3 \cdot H_2O$ (14 wt.%) was added dropwise to the above mixture under vigorous stirring for 1 h. The obtained products were separated by magnetic separation and washed to neutral using ultrapure water, and then dried under vacuum labeled as the dedoped Mt/PANI/Fe_3O_4. In order to realize the protonation of Mt/PANI/Fe_3O_4 composites, the products were treated with 0.1 M HCl, and then rinsed with water for several times before being dried in vacuum. In addition, the Mt/PANI/Fe_3O_4 composites with different contents of PANI and magnetic nanoparticles were also prepared, and the conditions of the sample preparation were summarized in Table 1. As a control, the products without magnetic nanoparticles (Mt/PANI) were also prepared under the same procedure without the addition of $NH_3 \cdot H_2O$, the conditions of the preparation were also presented in Table 1.

Table 1
The conditions of the samples preparation.

Samples	$FeCl_3 \cdot 6H_2O$/g	Clay	Aniline/mL	$NH_3 \cdot H_2O$/mL	[a]Molar ratio
Mt/PANI/Fe_3O_4-1	3.552	Mt	0.6	10	1:2
Mt/PANI/Fe_3O_4-2	3.552	Mt	1.2	10	1:1
Mt/PANI/Fe_3O_4-3	3.552	Mt	2.4	10	2:1
Mt/PANI/Fe_3O_4-4	3.552	Mt	3.6	10	3:1
Mt/PANI	3.552	Mt	1.2	0	1:1
VMT/PANI/Fe_3O_4	3.552	VMT	1.2	10	1:1

[a] Molar ratio of aniline to Fe(III).

In order to investigate the applicability of this scalable protocol to other two-dimensional clays (such as VMT), superparamagnetic VMT/PANI/Fe_3O_4 nanocomposites were also prepared, and the conditions of the preparation were shown in Table 1.

Table 1.

2.3. Adsorption of dyes

The adsorption experiments of Mt/PANI/Fe_3O_4 nanocomposites toward CR and the dedoped Mt/PANI/Fe_3O_4 nanocomposites toward three dyes (MB, BG and CR) were performed as follows: 25 mg of the as-prepared nanocomposites and 25 mL 100 ppm of MB, BG or CR were added into a series of conical flasks. The mixtures were shaken in a thermostatic shaker at 25 °C for 60 min, and then the adsorbents were separated by magnetic separation technique. The dye concentration in the solution was analyzed using ultraviolet (UV) spectrophotometer by monitoring the adsorption behavior at a wavelength of maximum absorbance (665 nm, 625 nm and 498 nm for MB, BG and CR, respectively). The adsorption ratio toward dyes was calculated from the dye concentrations in solutions before and after adsorption according to the following equation:

$$\text{Adsorption ratio} = \frac{c_0 - c_e}{c_0} \times 100\% \quad (1)$$

where c_0 and c_e were the initial concentration and the equilibrium concentration after adsorption of dye in aqueous solution, respectively.

In order to evaluate the adsorption process, the influence of the contact time and the initial concentration was investigated using the adsorption of the dedoped Mt/PANI/Fe_3O_4-2 toward MB as an example. In addition, the desorption and regeneration studies were also conducted. In a typical procedure, the adsorbents were separated and immersed into 25 mL of HCl (0.5 M) for 4 h after adsorption of MB, and then the adsorbents were washed with distilled water for several times and regenerated with NaOH solution (0.5 M) for 2 h. Next, the adsorbents were washed again with distilled water for several times and used for another adsorption process. The adsorption ratio toward MB was also calculated from the dye concentrations in solutions before and after adsorption.

2.4. Characterization

The X-ray diffraction (XRD) analysis was conducted with an X-ray powder diffractometer with Cu anode (PAN analytical Co. X'pert PRO), running at 40 kV and 30 mA. The morphologies of the samples were characterized with a JEM-1200 EX/S transmission electron microscope (TEM) (JEOL, Tokyo, Japan). The surface morphologies of Mt/PANI/Fe_3O_4-2 and VMT/PANI/Fe_3O_4 composites were observed using scanning electron microscope (SEM, JSM-6701F, JEOL, Ltd.). Bruker IFS 66 v/s IR spectrometer (Bruker, Karlsruhe, Germany) was used for the Fourier transform infrared spectroscopy analysis of the as-prepared samples in the range of 400–4000 cm^{-1} with the resolution of 4 cm^{-1}. Thermogravimetric analysis (TGA) of Mt/PANI/Fe_3O_4 nanocomposites

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