Microporous and Mesoporous Materials 256 (2018) 18–24

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

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

Investigation on the micro-structure and adsorption capacity of cellulosic biomass carbon based montmorillonite composite

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ARTICLE INFO

Article history:
Received 26 February 2017
Received in revised form
18 July 2017
Accepted 24 July 2017
Available online 26 July 2017

Keywords:
Biomass carbon
Montmorillonite
Composite
MB adsorption

ABSTRACT

Biomass derived amorphous carbon has received considerable attention in recent years for its great potential applications. In this work, the cellulosic biomass carbon based montmorillonite composite is synthesized by using carbon-bed pyrolysis method. The micro-structure and properties of samples are characterized by Raman, XRD, FT-IR, SEM, TEM and adsorption analyses. The results demonstrates that the montmorillonite components used to enhance the surface performance (granule-layer structure) also has strengthened the Methylene Blue adsorption capacity of biomass carbon in composite, the adsorption capacity is enhanced as the MT concentration increases, the maximum equilibrium value is obtained for 15 wt% montmorillonite mixed biomass carbon composite (93.5 mg/g), which confirms the effects of clay mineral (montmorillonite) on the biomass carbon in carbon-clay composite system. The isotherm data fits the Freundlich isotherm model ($R^2 = 0.927$) corresponding to the physical adsorption ($n = 1.214$, favorable adsorption). The kinetic data is well described by the intraparticle diffusion model ($R^2 = 0.939$), indicating the intraparticle diffusion controlled adsorption process.

1. Introduction

Globally escalating pressures for both environmental crisis and energy shortage have raised wide concerns about the potential to find facile, abundant, environmentally beneficial and nontoxic materials [1]. Biomass is a superior raw material for synthesizing valuable carbon materials as its high quality and huge amount of environmental friendly renewable resources [2]. Renewable resources can represent a means of developing a sustainable development strategy in view of the current excessive consumption of fossil resources and the attendant global warming [4]. The biomass carbon has received considerable attentions in recent years for its great promising applications as adsorbent materials, hydrogen storage, biochemicals and others to benefit the humanity [3]. Herein, cellulose is an abundant, renewable and biodegradable raw material derived from natural biomass [4]. As the adsorption techniques for wastewater treatment have become more popular in recent years owing to their efficiency in the removal of pollutants than other conventional methods, the cellulose derived biomass carbon represents a potential resource for the replacement of qualified adsorbents [5].

Montmorillonite, among the most studied clay minerals, possesses expandable-layered silicates consists of one octahedral and two tetrahedral unit forming a platelet approximately 10 Å thick [6]. Due to the specific layered structure, high surface area and high ion exchange capacity, montmorillonite has great potential for a wide range of applications such as adsorption, catalysis, and contaminant removal [7]. One important property is that the layered structure is negatively charged, the charge is normally balanced by hydrated cations placed in the interlayer spaces, which can effectively remove some inorganic and organic pollutants from aqueous solutions [8,9]. Montmorillonite clay is believed to be a low-cost, naturally abundant and green material that have been widely applied in remediation of various contaminants in aqueous solution [10]. Nevertheless, montmorillonite with very fine particles is unsuitable as fixed-bed media or flocculation additives in water treatment facilities [11].

In this work, we have designed and prepared the eco-friendly biomass carbon based montmorillonite composites by carbon-bed pyrolysis method from green cellulosic biomass. The as-prepared carbonaceous composite exhibits high efficiency for the removal of cationic dyes from aqueous solution. In addition, the adsorption

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http://dx.doi.org/10.1016/j.micromeso.2017.07.052
1387-1811/

kinetics and isotherms of the organic dyes onto the obtained carbonaceous composite have also been investigated. The research confirms the great influences of montmorillonite clay mineral on biomass carbon in carbon-clay composite system, the prepared biomass carbon based montmorillonite composite has the potential to be explored as an efficient and benign adsorbent, which may provide new ideas for exploiting new carbonaceous composite and be conducive to high efficient utilization of natural biomass and mineral resources.

2. Experimental

The cellulosic biomass carbon based montmorillonite (MT) composites were synthesized by carbon-bed pyrolysis method. The purity of adopted MT (Panshi, China) was above 99%, and the whiteness was >89%. The carboxy methyl cellulose ($[C_6H_7O_2(OH)_2CH_2COONa]_n$, YANXING CHEMICAL, China) was adopted as raw material for biomass, the viscosity of CMC was 900–1200 mPa s. The raw materials with various MT concentrations (0, 5, 10, 15 and 20 wt%) were ball-milling for 12 h to ensure the uniformity. Then the precursors were poured into small crucibles (30 mL, high alumina) which were covered by small crucible covers, the covered cucibles surrounded by active carbon blocks were centered at the bottom of a covered crucible (500 mL). Finally, the samples were hypoxia calcined in high temperature furnace (temperature: 400 °C, constant time: 4 h, heating rate: 8 °C/min) to prepare various samples (CMC, 5-MT-CMC, 10-MT-CMC, 15-MT-CMC and 20-MT-CMC).

The Raman spectra analysis of composite samples was conducted using Raman microscope (inVia, UK) with a laser of 532 nm wavelength at 0.2 mW. The X-ray diffraction measurement (DX-2700, China) was carried out to characterize the crystalinity of composites, the X-ray tube which uses a Cu target is working at the power of 35 kV and 25 mA. The Fourier transform infrared (FT-IR) spectra analysis of samples were examined using a Fourier transform infrared spectrometer (NICOLET380, USA) from 4000 to 400 cm^{-1} with a spectral resolution of 4/cm. The Scanning electron microscopy (SEM) analysis of samples was examined using Scanning electron microscope (JSM-6700F, Japan, 15 keV). The Transmission electron microscopy (TEM) analysis of samples was carried out with Transmission electron microscope (JEM-2100F, Japan) operated at 200 keV. The N_2 adsorption-desorption isotherms of samples are measured on a specific surface and pore size analyzer (JW-BK222, China) at liquid nitrogen temperature (77 K), each sample is outgassed at 150 °C until a stable vacuum of 3×10^{-3} Torr is reached.

The adsorption experiments are measured by 30 mL of a 30 mg/L Methylene Blue (MB, $C_{16}H_{18}ClN_3S \cdot 3H_2O$, 373.90 g/mol) aqueous solution (pH 7.5) with 10 mg of adsorbents. The aqueous solutions are shaken at 120 rpm equivalent shaking rate for 1 h (room temperature) by using an oscillator (HY-4, China). After keeping in dark place for 12 h to allow the adsorbents settled, at which time the supernatant is collected and characterized by using the UV-vis spectrophotometer (T6-NC, China), which is performed on a spectroscopy at the wavelength of 664 nm. The equilibrium adsorption capacity, Q_e (mg/g), is calculated by using the following equation:

$$Q_e = \frac{(C_o - C_e)V}{M} \quad (1)$$

where C_o and C_e (mg/L) are the initial and equilibrium concentrations of MB aqueous solution, respectively; V (L) is the volume of the solution; and M (g) is the mass of used adsorbent [11].

The adsorption of MB onto the composite is also evaluated at constant temperature (25 °C) for the investigation of adsorption isotherms, which is simulated by using the Langmuir and Freundlich model [12]. The kinetic experiments are basically identical to the equilibrium tests, the aqueous solutions are measured at present time intervals (1–10 h), and the concentrations of MB (10–100 mg/L) are similarly tested. The adsorption capacity at time t (h), Q_t (mg/g), is calculated by using the following equation:

$$Q_t = \frac{(C_o - C_t)V}{M} \quad (2)$$

where C_t (mg/L) are the concentrations of MB solution at any time t [13–15].

3. Results and discussion

Typical Raman spectra of as-prepared samples at the range from 1000 cm^{-1} to 2000 cm^{-1} are presented shown in Fig. 1. All carbonaceous samples display strong peaks around 1370 and 1602 cm^{-1}, assigned to the D and G band, respectively. The G band is the characteristic peak for the E_{2g} symmetry stretching vibration of carbon sp^2 bonds (ordered structure) in a hexagonal lattice, whereas the D band is the characteristic peak for the A_{1g} symmetry vibration of carbon atoms with dangling bonds (structural defects) in an amorphous carbon network [16]. The integrated intensity ratios of the D band to G band (I_D/I_G) reflect the degree of graphitization for each sample. The original CMC sample presents the highest structural integrity as indicated by the lowest I_D/I_G value (0.5598), presenting the great in-plane sp^2 domains of amorphous carbon [17]. Meanwhile, the carbonaceous composites display the increasing I_D/I_G values of 0.6778 (5-MT-CMC), 0.7514 (10-MT-CMC), 0.7856 (15-MT-CMC) and 0.7249 (20-MT-CMC), respectively. It is generally assumed that the introduction of MT component used to enhance the surface performance also induce unavoidable damages to the ordered carbon structure.

Fig. 2 shows the XRD patterns of CMC, biomass carbon based MT composites and MT samples. The derived CMC gives the XRD pattern with broad diffraction peaks in the 2theta region of 20–25°, corresponding to the amorphous carbon structure related to the diffraction of disordered graphitic phase [18]. Upon mixture of MT composition, the carbon peaks of composite are suddenly weakened assigned to the crystal interference. While the MT concentration is increasing, the (100) diffraction peak of montmorillonite phase is displayed in the 15-MT-CMC pattern [19]. The

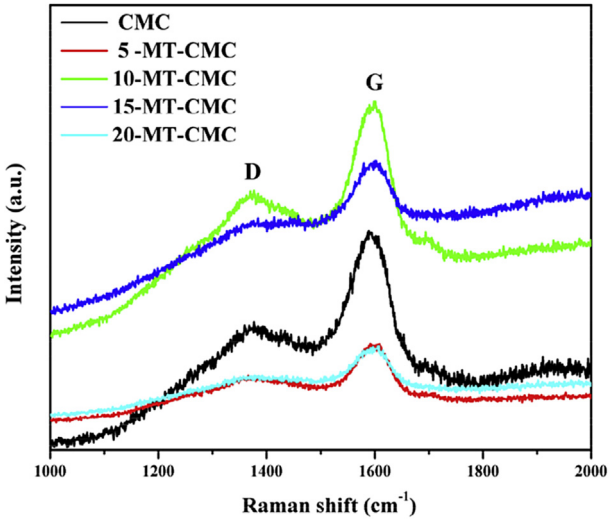

Fig. 1. Raman spectra of CMC and biomass carbon based MT composites.