



Biomass derived palygorskite–carbon nanocomposites: Synthesis, characterisation and affinity to dye compounds



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ABSTRACT

Clay minerals can act as a uniform dispersion medium for nano-sized carbon particles. However, literature on the preparation and characteristics of palygorskite–carbon nanocomposites is scant. Using a hydrothermal carbonisation technique this study developed two nanocomposites on fibrous palygorskite from starch: the first without a post-synthesis treatment (Composite 1); and the second with an activation at 550 °C for 3 h (ramp at 10 °C min⁻¹) under CO₂ environment (200 mL min⁻¹) (Composite 2). A uniform dispersion of nano-scale carbon spheres was formed on partially destroyed palygorskite structures. Composite 2, which indicated the formation of graphitised carbon nanoparticles, generated a 17-fold greater specific surface area than Composite 1 and also created micro- and mesopores in its structure. The nanocomposites, especially in Composite 1, contained organic surface functional groups (C–H, C=C, C=O) and indicated variable affinity to cationic and anionic dye compounds. While Composite 2 adsorbed a larger amount of anionic orange II dye (23 mg g⁻¹), Composite 1 adsorbed more cationic methylene blue (46.3 mg g⁻¹). Isothermal and kinetic modelling of the adsorption data indicated that in addition to electrostatic attraction for methylene blue adsorption on both nanocomposites, a pore diffusion mechanism was involved and the boundary resistance was greater for orange II than methylene blue adsorption. Being a material developed from green biomass (starch) and an abundant natural resource (palygorskite), these nanocomposites have immense potential for application in environmental remediation including in situ immobilisation of contaminants in soil.

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1. Introduction

Clay minerals have wide potential applications for treating environmental contaminants. Due to their unique properties such as layered structures, large surface areas, high cation exchange capacity (CEC) and enormous environmental stability, clay minerals are a popular choice for cleaning diverse organic and inorganic pollutants in the environment (Churchman et al., 2006; Sarkar et al., 2012b). Worldwide availability and hence low cost also make these minerals appropriate for environmental applications. Both naturally occurring clay minerals and their modified products can be used for treating contaminated water, soils and air. Modification of clay minerals by physical, chemical

or biological processes improves their efficiency in removing contaminants many-fold (Churchman et al., 2006).

Among the various clay modifications, anchoring of carbonaceous materials, which are abundant in oxygen-containing groups and exist on the surface of solid adsorbents such as clay minerals, has emerged as a new class of adsorbent for contaminant removal (Anadão et al., 2011, 2014; Chen et al., 2011; Kumar et al., 2011; Ai and Li, 2013). Clay minerals or zeolite can act as a uniform dispersion medium for nano-sized carbon particles and thus ideally help improve the composite's reactivity to target pollutant compounds (Katsuki et al., 2005; Anadão et al., 2011; Wu et al., 2014). Uniform dispersion of carbon nanoparticles onto a suitable support is required in order to apply the composite under in situ conditions. This can refer, for example, to the remediation of contaminated ground water because such a composite largely prevents: (a) nanoparticle agglomeration; and (b) unwanted displacement from the target site. Other high end applications of carbon–clay mineral materials include catalysis, biocatalyst support, adsorbents for chromatography and haemosorbents in medicine (Anadão et al., 2011).

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Clay–carbon composite material can be synthesised by pyrolysis of a carbon precursor hosted on the clay surface or intercalated in the clay layers. However, this process involves large energy consumption and extreme heat that can destroy clay minerals' crystalline structure. Also, increased awareness about sustainable and green nanotechnology has made the development of clay–carbon nanocomposite from renewable green precursors critical. The hydrothermal carbonisation (HTC) process has recently proved to be effective for clay–carbon nanocomposite synthesis using biomass carbon precursor (Hu et al., 2010; Chen et al., 2011; Li et al., 2012; Zhang et al., 2014). This is considered to be a greener approach because it consumes less energy (carbon deposits at low temperature) and uses renewable carbon precursors such as glucose, sucrose and cellulose. Since carbon nanoparticle deposition takes place at a comparatively lower temperature in the HTC process compared to carbon nanotube synthesis in the high-temperature chemical vapour deposition (CVD) technique, the former provides numerous oxygen-containing groups to the nanocomposite surfaces (Qian et al., 2006; Li et al., 2012, 2014). Consequently it would be a good adsorbent for water purification (Xu et al., 2008).

The properties of clay–carbon nanocomposites would depend on both the clay mineral characteristics and carbon precursor type. Since palygorskite is a non-swelling type clay mineral, its carbon nanocomposite may impart greater permeability than a swelling montmorillonite composite for removing contaminants under flow conditions when used in a barrier (Sarkar et al., 2010a, 2012a). However, information on the preparation and characteristics of palygorskite–carbon nanocomposites is scarce in the literature (Chen et al., 2011; Wu et al., 2011; Liu et al., 2013). Therefore, this study aims to: firstly, develop nanocomposites from starch using fibrous palygorskite; and secondly, characterise the products and study their affinity to organic dye compounds (orange II and methylene blue) in aqueous solutions. Removing dye compounds from contaminated water is important because many of them are toxic, carcinogenic and can damage the environment and human health (Sarkar et al., 2011; Ai and Li, 2013).

2. Experimental section

2.1. Materials and reagents

A palygorskite (Grade 050F) originally from Western Australia was supplied by Hudson Resources Limited and was used as received, without further purification. The CEC of this clay mineral was 17.0 cmol (p^+) kg^{-1} and it had a specific surface area of 89 $m^2 g^{-1}$. Sodium exchanged palygorskite was prepared by dispersing 20 g clay in 1 L of 1 N NaCl (Sigma-Aldrich) solution. The mixture was agitated on a magnetic stirrer at room temperature for 48 h, following which the sediment was separated through centrifugation at 15,000 rpm for 10 min. The sediment was washed 4 times with deionised water, dried at 60 °C, ground into powder and stored in an air tight container. Soluble starch was used as the renewable carbon precursor and zinc chloride ($ZnCl_2$) served as the catalyst for carbon deposition (both supplied by Merck Pte Ltd, Singapore). The dye compounds: orange II (4-(2-hydroxy-1-naphthylazo) benzenesulfonic acid sodium, $C_{16}H_{11}N_2NaO_4S$, MW: 350.33), and methylene blue (3,7-bis(dimethylamino)phenazathionium chloride, $C_{16}H_{18}ClN_3S \cdot 3H_2O$, MW: 373.90), were supplied by Sigma-Aldrich, Australia.

2.2. Preparation

Carbon nanocomposites were synthesised using the HTC method (Chen et al., 2011). In a typical procedure, 15 g starch was dissolved in 200 mL suspension containing 3 g sodium–palygorskite in deionised water at 50 °C by stirring it magnetically for 3 h. A gel was formed and separated by filtration through Whatman No. 1 filter paper. Zinc chloride (zinc equivalent to 400% CEC of the palygorskite) was added to the gel and mixed homogeneously. The mixture was then transferred

to a Teflon lined hydrothermal bomb and sealed properly. It was kept in a pre-heated oven at 250 °C for 3 h. Following cooling, the material was heat activated under two conditions: (1) heated at 105 °C in an oven for 3 h in presence of air (Composite 1); and (2) heated at 550 °C for 3 h (ramp at 10 °C min^{-1}) under CO_2 environment (200 mL min^{-1}) (Composite 2).

2.3. Materials characterisation

2.3.1. Surface area and pore size distribution

N_2 adsorption–desorption experiments were performed at liquid nitrogen temperature (-196 °C) on a Micromeritics Gemini 2380 surface analyser. Samples were outgassed at 70 °C for 12 h under high vacuum. Specific surface area was determined with the Brunauer–Emmett–Teller (BET) method and microporous volume was evaluated using the t-plot method. Average pore diameter was estimated via the Barrett–Joyner–Halenda (BJH) method.

2.3.2. X-ray diffraction (XRD)

Powdered nanocomposite samples were pressed in stainless steel sample holders for XRD analysis. XRD patterns of the nanocomposites were acquired using $CuK\alpha$ radiation ($\lambda = 1.5418$ Å) on a PANalytical, Empyrean X-ray diffractometer operating at 40 kV and 40 mA between 5 and 80° (2θ) at a step size of 0.016° (100 s scan step time) with a fixed 0.5° divergence slit and 1° anti-scatter slit. The basal spacing was calculated from the 2θ value using Bragg's equation, $n\lambda = 2d \sin\theta$.

2.3.3. Scanning electron microscopy (SEM)

Nanocomposite samples were fixed on a double-sided tape, and coated with 20 nm of carbon or 5 nm platinum by evaporation using a Quorum QT150ES coating system. Samples were examined using a FEI Quanta 450 FEG Environmental Scanning Electron Microscope equipped with an EDAX Apollo EDX detector. Images were taken in high vacuum mode and with a 20 kV accelerating voltage using an Everhart–Thornley Detector (ETD) and a solid state Back Scattered Electron detector (BSED). EDAX spectra, X-ray maps and line-scans were acquired for selected areas on the samples. EDAX maps were acquired overnight; line scans were derived from the EDAX maps. EDAX point spectra were acquired for 100 s at a point.

2.3.4. Transmission electron microscopy (TEM)

Nanocomposite samples were mounted on copper grid and observed under a JEOL JEM – 2100F Transmission Electron Microscope with a 200 kV accelerating voltage.

2.3.5. Particle size

The palygorskite and nanocomposites were suspended in 0.1 M NaCl solution, agitated for 24 h on an end-over-end shaker and ultrasonicated for 30 min. Size of the uniformly dispersed particles was determined by using a Nicomp™ 380 DLS Particle Sizer.

2.3.6. Fourier transformed infrared spectroscopy (FTIR)

The nanocomposite samples (about 1% w/w) were ground and mixed homogeneously with dehydrated KBr and pressed into discs for FTIR analysis. Infrared (IR) spectra were obtained using an Agilent Cary 600 Series FTIR Spectrometer. Spectra over the 4000–400 cm^{-1} range were obtained by the co-addition of 64 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 $cm s^{-1}$.

2.3.7. Raman spectroscopy

The nanocomposites were incubated statically on a silicon wafer. Raman spectra were collected by a WITec Confocal Raman Microscope (Alpha 300RS, Germany) equipped with a 532 nm laser diode (<60 mW). A CCD detector (cooled to approximately -60 °C) was used to collect Stokes Raman signals under a 100× objective (Nikon) at room temperature over the wavenumber range of 0–2500 cm^{-1} .

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