



# Facile and green fabrication of magnetically recyclable carboxyl-functionalized attapulgite/carbon nanocomposites derived from spent bleaching earth for wastewater treatment

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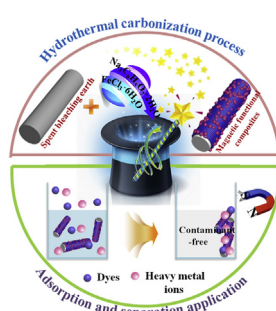
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## HIGHLIGHTS

- Magnetic attapulgite/carbon nanocomposites decorated with carboxyl groups were prepared.
- Composition and properties of nanocomposites were depended on the concentration of sodium citrate.
- Maximum adsorption capacity for MB and Pb(II) reached 254.83 mg/g and 312.73 mg/g, respectively.
- This strategy provided a novel avenue to fully utilize spent organic-matter-rich clay waste.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A facile and green hydrothermal approach was employed to fabricate the magnetic carboxyl-functionalized attapulgite/carbon nanocomposites based on the spent bleaching earth. The preparation process simultaneously involved the growth of magnetic nanoparticles and the coating of carbon species with carboxyl groups on the surface of attapulgite via hydrothermal redox reactions between Fe(III) and sodium citrate in the aqueous solution. The composition, magnetic response as well as adsorption properties of as-prepared nanocomposites could be facily controlled by adjusting the concentration of sodium citrate. The resultant adsorbents possessed fast adsorption kinetics and the maximum adsorption capacity toward MB and Pb(II) could reach 254.83 mg/g and 312.73 mg/g while the concentration of sodium citrate was 0.6 M. In addition, the adsorbent could be easily recycled due to its magnetism and the adsorption capacity had a slight decrease after six adsorption-desorption cycles. All the information revealed that the carboxyl-functionalized attapulgite/carbon nanocomposites were expected to be a promising candidate for high-efficient removal of contaminants from wastewater in future practical use.

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## 1. Introduction

Clay/carbon composites are exploited to be applied in different fields owing to the favorable physical and chemical properties and good environmental compatibility [1,2]. Compared with conventional carbonaceous materials, the combination of clay minerals and carbon species can fulfill an affordable composite to remove

various contaminants from wastewater [3,4]. However, the adsorption capacity of clay/carbon composites toward pollutants is also restricted due to the scarcity of functional groups and the defect inherited from the feedstock. In addition, it was time-consuming and uneconomic to separate those adsorbents from the treated water via traditional centrifugation or filtration for recycling owing to the small size [5,6]. Therefore, magnetically functionalized clay/carbon composites have received increasing attention due to the easy separation from solution for recycling by an external magnetic field [7].

In general, three common methods are used to synthesize magnetic materials, i.e. the pyrolysis of pre-saturation of feedstock in iron precursor, chemical co-precipitation  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  in inert atmosphere, and solvothermal treatment of  $\text{Fe}^{3+}$  in ethylene glycol [8,9]. The incorporation of magnetic particles into carbonaceous materials also can be realized by above strategies. Mubarak et al. prepared magnetic biochar from a  $\text{FeCl}_3$ -impregnated palm oil empty fruit bunch by microwave heating technique, and the magnetic composites exhibited a maximum adsorption capacity of  $265 \text{ mg g}^{-1}$  to methylene blue due to the high surface area of  $890 \text{ m}^2 \text{ g}^{-1}$  [10]. Gu et al. synthesized magnetic carbon nanoadsorbents from the annealing of functionalized polystyrene with an iron salt in a nitrogen atmosphere to investigate adsorption affinity to aqueous tetrabromobisphenol A [11]. Sun et al. developed a  $\text{Fe}_3\text{O}_4$ -coated biochar via chemical co-precipitation of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  for adsorption of crystal violet [12]. However, these methods are limited in the practical application due to the complicated process, the use of the organic solvent and the low adsorption capacity. It is indispensable to develop a facile and green approach for fabrication of magnetic carbonaceous materials with high adsorption capacity to pollutants [13].

In fact, the choice of the carbon source is also a crucial factor determining the adsorption properties and the production cost of magnetically functionalized carbonaceous materials, and the main factors include the type and the cost of carbon source. However, it is impractical to remove pollutants from water using magnetically functionalized carbonaceous materials for large scale application in most cases due to the employment of the costly precursors, such as graphene oxide, carbon nanotubes, glucose, starch and commercially available cellulose [8,14–18]. Spent bleaching earth (SBE), a waste by-product, is derived from refining process of crude edible oil. Owing to the residual of organic matters, it can be regarded as a prospective and valuable carbon precursor for preparation of clay/carbon composites, as described in our previous study [19,20]. To the best of our knowledge, few studies are presented regarding the application of SBE for constructing magnetically functionalized clay/carbon nanocomposites.

In this study, the magnetic carboxyl-functionalized attapulgite/carbon (CFAC) nanocomposites were prepared by one-pot hydrothermal method in the presence of sodium citrate for the high-efficient removal of toxic dyes and heavy metal ions. The change of crystalline phase and adsorption properties of CFAC with the sodium citrate concentration were investigated in detail. The effect of the critical factors including pH, contact time and initial concentration of pollutants on the adsorption properties were also systematically studied. Furthermore, a feasible adsorption mechanism of CFAC toward dyes and heavy metal ions was also proposed based on the experimental evidence.

## 2. Experimental

### 2.1. Materials

The spent bleaching earth (SBE), which was mainly composed of attapulgite (APT) and about 22.3% of organic matters (such as

grease, natural pigment, fatty acid, etc.), was provided by The W clay Industries Sdn Bhd (Malaysia) [19]. Methylene blue (MB, molecular formula:  $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$ ) and lead acetate ( $\text{Pb}(\text{CH}_3\text{COO})_2$ ) were received from Shanghai Sinopharm Chemical Reagent Co., Ltd., China. Ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), sodium acetate ( $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ ), sodium citrate ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ ) and other reagents were all of analytical reagent grade from Tianjin Kermel Chemical Reagent Co., Ltd., China. All chemicals were used as received without further purification. Ultrapure water used in experiments had a resistivity of  $18.25 \text{ M}\Omega \text{ cm}$ .

### 2.2. Fabrication of CFAC nanocomposites

The fabrication of CFAC nanocomposites were performed by one-pot hydrothermal route. The detailed procedure was as follows: 2.0 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 5.0 g of  $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$  were dissolved in 60 mL deionized water to form a clear solution. And then sodium citrate was added with the concentration of 0.05 mol/L, 0.1 mol/L, 0.2 mol/L, 0.4 mol/L, 0.6 mol/L and 0.8 mol/L under vigorous magnetic stirring for 30 min. Next 0.6 g SBE was ultrasonically dispersed into the above dispersion for 30 min to form a homogeneous precursor. Finally, the above mixture was sealed in a Teflon-lined stainless steel autoclave (100 mL capacity) and the temperature was maintained at  $200^\circ \text{C}$  for 12 h. The obtained solid product was washed with deionized water and ethanol in sequence after being cooled to room temperature, and dried in a vacuum oven at  $60^\circ \text{C}$  for 12 h. The as-prepared samples in the presence of sodium citrate were designated as CFAC-x, where x was the initial sodium citrate concentration as above described.

As a control, a similar preparation method was used to synthesize the products without sodium citrate and Fe(III), or sodium citrate, and the sample were marked as APT/C and CFAC-0, respectively. The detailed preparation conditions for all samples were listed in Table S1 in the Supporting Information. Besides, the change of pH value before and after the hydrothermal reaction was monitored using a pH-meter (FE20, Mettler Toledo, Switzerland), as shown in Table S2.

### 2.3. Characterization

Surface functional groups were determined by Fourier transform infrared (FTIR) spectra and were recorded on a Fourier transform infrared spectrometry (Thermo Nicolet NEXUS TM, USA) using KBr pellets. The spectra were recorded from 4000 to  $400 \text{ cm}^{-1}$  and were presented at transmittance mode. The microscopic morphology was observed using JSM-6701F Field Emission Scanning Electron Microscope (FESEM) (JEOL, Tokyo, Japan) at an acceleration voltage of 10.0 kV and a working distance of 10 mm at high vacuum mode after coating the sample with gold film. High resolution transmission electron microscopy (HRTEM, JEM-2010, JEOL, Tokyo, Japan) images were obtained at an acceleration voltage of 200 kV, and the sample was ultrasonically dispersed in anhydrous ethanol and dropped onto a grid before observation. The X-ray diffraction (XRD) patterns were conducted with an X-ray power diffractometer with a  $\text{Cu K}\alpha$  ( $1.540598 \text{ \AA}$ ) radiation from  $3$  to  $80^\circ$  ( $2\theta$ ) at a scan rate of  $0.05^\circ \text{ s}^{-1}$ , running at 40 kV and 30 Ma (X'Pert PRO, PAN analytical Co., Netherlands). The zeta potentials of suspensions were measured on a Malvern Zetasizer Nano system with irradiation from a 633 nm He-Ne laser (Malvern Zeta voltmeter, ZEN3600, Britain). The aqueous suspension (0.5%, w/v) for measurement was prepared by dispersing the samples into deionized water under ultrasound. Magnetic properties of CFAC nanocomposites were detected by vibrating sample magnetometer (Lakeshore 7304). The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method and the pore volume was

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