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One-step synthesis of amino-functionalized attapulgite clay nanoparticles adsorbent by hydrothermal carbonization of chitosan for removal of methylene blue from wastewater

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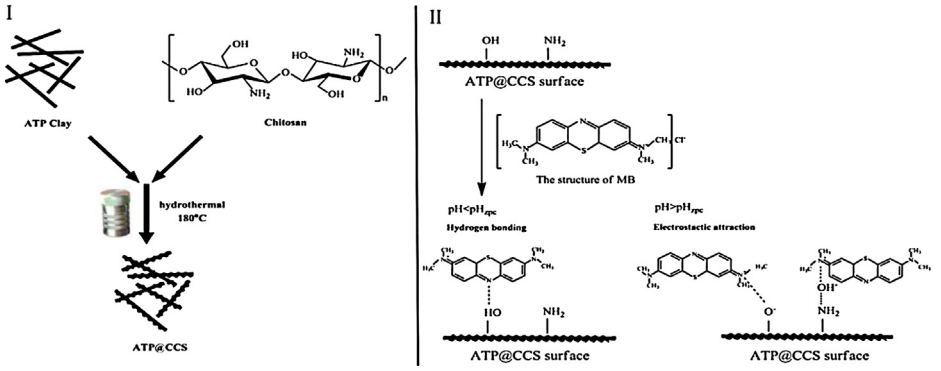
HIGHLIGHTS

- A green synthesis strategy of one-step HTC process was developed for the preparation of ATP@CCS adsorbent.
- Two low-cost, ecofriendly materials (i.e., ATP, rich in nature and chitosan, a cheap, green chemical) were used as raw material.
- The maximum adsorption capacity could be up to 226.24 mg g^{-1} at 318.15 K.
- The presence of ionic strength had no significant effect on the MB adsorption.
- The ATP@CCS could be regenerated easily and reused for five times without visible loss of its original capacity.

GRAPHICAL ABSTRACT



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ABSTRACT

A new kind of amino-functionalized attapulgite clay nanoparticle adsorbent (ATP@CCS) was fabricated by hydrothermal carbonization of chitosan at a mild temperature and their application for the Methylene Blue (MB) removal from wastewater was studied in this work. Characterization of material was examined by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscope (SEM) and zeta potential analysis. The adsorption properties of the ATP@CCS was investigated as a function of pH of solution, ionic strength, contact time, initial concentration of MB and temperature. It is revealed that the composites pretreated in the solution with higher pH value exhibited larger adsorption capacities. The ionic concentration in MB solution slightly impacted the removal of MB by the ATP@CCS composite. Kinetic studies showed that the composites could adsorb MB rapidly and reached the equilibrium in 120 min, the adsorption process followed pseudo second order kinetics and involvement of particle diffusion mechanism. Adsorption isotherms indicated that Langmuir model was more suitable than the Freundlich model for well elucidation of the experimental data, the calculated maximum adsorption capacity could be up to 215.73 mg g^{-1} at 318.15 K. Moreover, thermodynamic analysis indicated an exothermic nature of adsorption and a spontaneous and favorable process. Regeneration experiments

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revealed that the ATP@CCS could be regenerated easily and reused for five times without visible loss of its original capacity. The study suggests that the ATP@CCS is a promising adsorbent for removal of cationic dyes from aqueous solution.

1. Introduction

The effluents of wastewater in many industries such as food, paper, carpets, rubbers, plastics, cosmetics, textiles, etc., contain various kinds of synthetic dyestuffs [1]. Concern exists since the discharge of these wastes into receiving waters causes severe damages to the environment and a very small amount of dye in water is highly visible and undesirable [2–4]. Therefore, it is important to treat the dye-contaminated water before discharge to protect the environment and ecosystem. Many technologies have been developed for dye removal from aquatic environments, including physical, chemical, and even biological approaches [5,6]. However, chemical and biological methods are very effective for the treatment of contaminated water but they leave huge amount of by-products [7,8]. In contrast, adsorption techniques as a physical approaches is regarded to be a reliable treatment approach due to its low capital investment, abundant raw material source, simple in design and operation, and non-toxic [9–11], wherein development of high-quality adsorbents is the key.

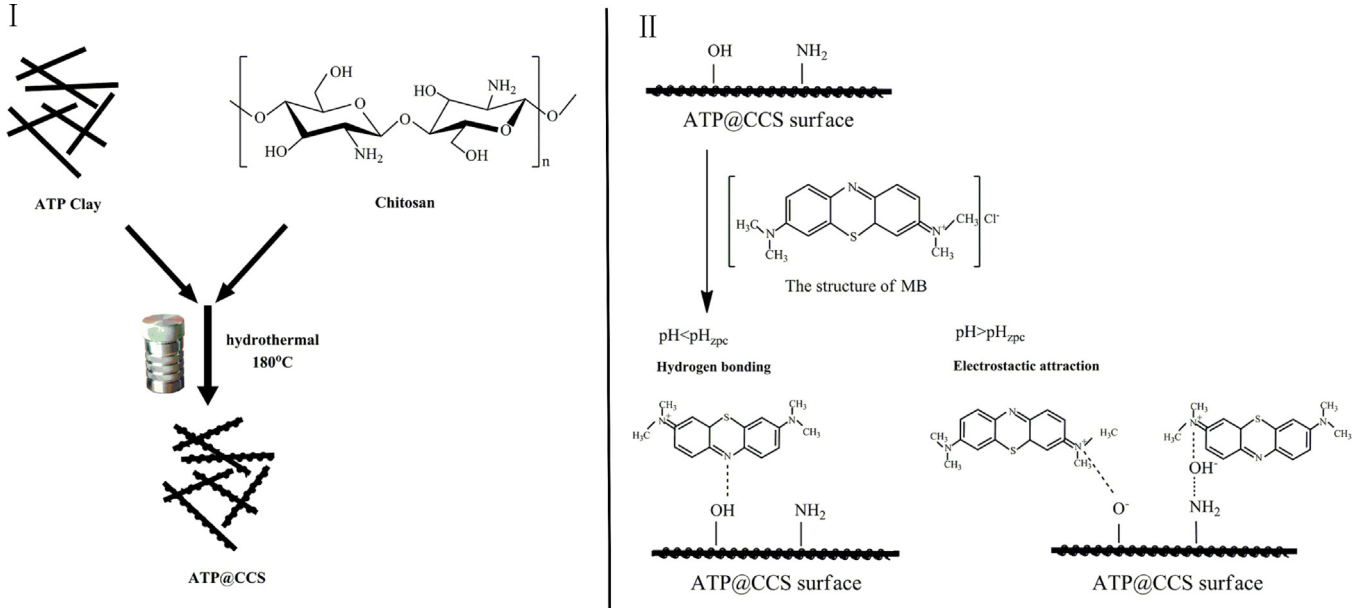
Nevertheless, there are certain disadvantages in the present reported adsorbents, such as the use of environmentally unfriendly reagents (i.e., poisonous solvents, surfactants, or catalysts) in synthetic process, the complicated preparation methods, and the lower adsorption capacity [12–14]. Therefore, it is urgent to develop a green synthesis strategy for the preparation of cheaper and more environmentally acceptable adsorbents for water decontamination.

Recently, a green synthetic method, the so-called hydrothermal carbonization (HTC) process, has been developed to obtain a series of functional carbon-based nanomaterials from biomass [15–18]. Compared to the carbon nanotubes, a hot material for removal of contaminants [19,20], produced by high-temperature CVD techniques, the carbonaceous materials obtained from the HTC process at lower temperature possessed numerous oxygen-containing groups on their surfaces and hence could have remarkable feature to be used as adsorbents for water purification [18,21]. Based on that, we chosen the chitosan as potential precursors within this process creatively instead of saccharides such as glucose, sucrose, starch and cellulose reported in many studies [22–24] due to an abundant amino functional groups in its structure. A new kind of attapulgite clay@ carbonized chitosan (ATP@CCS) nanocomposite adsorbent was prepared via the one-step HTC synthesis route at a mild temperature (180 °C), in which ATP plays the role as a template (low-cost and rich in nature) and the carbonization and functionalization will occur through the dehydration of the chitosan, leading to the formation of highly amino-functionalized carbonaceous shell coating the ATP. The synthetic procedure is illustrated in Scheme I. The obtained ATP@CCS nanocomposite exhibited a high adsorption capability for methylene blue (MB). To evaluate the adsorption performance, a batch adsorption experiment was conducted systematically and the adsorption mechanism was studied according the analysis of effect of solution pH. Furthermore, the adsorption kinetics, isotherms, thermodynamics and reusability of ATP@CCS nanocomposite were also investigated.

2. Materials and methods

2.1. Materials and chemicals

The ATP clay was kindly supplied by Jiu Chuan Clay-Technology Co., Ltd. (Jiangsu Province, China) and was milled into about 320 mesh. All other chemicals were analytical grade and commercially available from Shanghai Chemical Reagent Co. Ltd. and used as received without further purification.



Scheme 1. I. Schematic illustration of the synthesis procedure of the ATP@CCS nanocomposite and II. The plausible mechanism for the removal of and MB from aqueous solution.