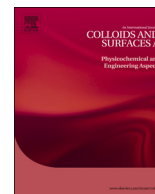




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## A novel polyalcohol-coated hydroxyapatite for the fast adsorption of organic dyes

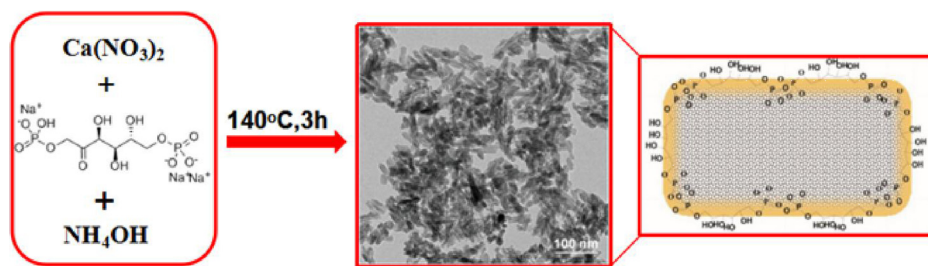


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### GRAPHICAL ABSTRACT



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### ABSTRACT

Surface-modified hydroxyapatite (HA) nanocomposites have been synthesized from D-fructose-1,6-phosphate trisodium salt octahydrate (DFP) via a simple and green hydrothermal process. Comprehensive X-ray powder diffraction (XRD), Transmission electron microscopy (TEM), Scanning electron microscopy (SEM), Thermal gravimetric analysis (TGA), Fourier transform infrared (FT-IR) and solid state nuclear magnetic resonance (SSNMR) characterizations revealed that the HA nanocomposite adopt a rod-like core/shell morphology in which the inorganic HA core is covered with an organic shell of polyalcohol species. The HA nanocomposite exhibits a large surface area of 203.18 m<sup>2</sup>/g, and enhanced adsorption capacities of organic dyes such as Methyl orange (MO) and Congo red (CR). Remarkably, the adsorption processes were particularly fast in which the equilibriums are reached within minutes. The adsorption kinetics can be well described by a pseudo-second-order kinetic model. These experimental results demonstrated that such HA nanocomposites are promising adsorbents for the efficient removal of organic dyes from water.

### 1. Introduction

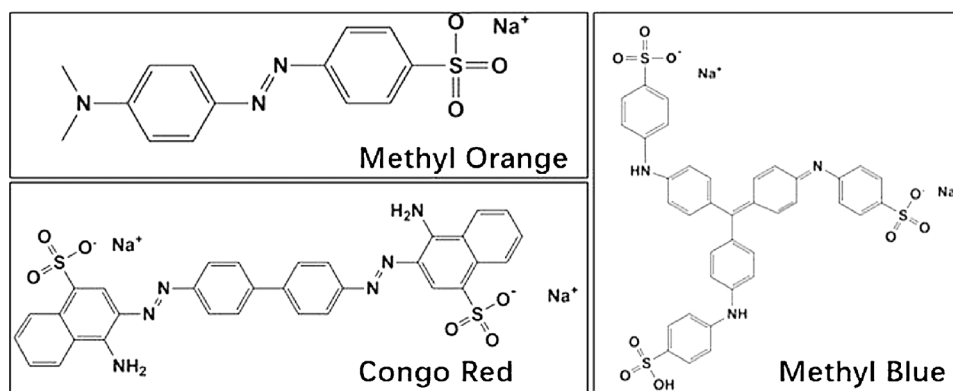
Considerable amount of organic dyes such as methyl blue, methyl orange etc. are present in industrial effluents discharged into natural water systems. These dyes have become a serious environmental concern because they could deleteriously affect the photosynthetic aquatic

life [1–3]. Since many organic dyes are resistant to heat, light or oxidizing agents, treatment via adsorption is often favored due to its highly efficiency, wide applicability and cost-effectiveness [4–6]. A large variety of materials such as clays [7], hybrid fibers [8], activated carbons [4], zeolites [9], etc. may be utilized as adsorbents, some of which show excellent adsorption capacity. However, for many reported

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**Scheme 1.** The molecule structures of Methyl orange (MO), Congo red (CR) and Methyl blue (MB).

adsorbents, the adsorption process takes tens of minutes or even hours to reach equilibrium [10–12], which greatly hampers their practical applications. It is challenging to design novel adsorbents which possess both high adsorption capacity and rapid rate, and at the same time meet the standards of low cost and minimal environmental impact.

With the above mentioned considerations, many researches focused on hydroxyapatite (HA),  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , a bio-compatible calcium phosphate material with significant importance in chemistry and biology [13,14]. HA has been shown to be a promising adsorbent due to its ionic exchange ability against heavy metal ions and reasonable affinity towards certain dyes [15,16]. However, the adsorption capacity and, in particular, the adsorption rate is relatively low for most HA materials. In this work, we developed surface-modified HA nano-rods using D-fructose-1,6-phosphate trisodium salt octahydrate (DFP) as the phosphorus source via a simple hydrothermal process using water as the solvent. We demonstrated that the HA nano-rods possess a surface organic layer rich in hydroxyl groups, which can dramatically enhance the adsorption of certain dyes such as methyl orange (MO), Congo red (CR) and methyl blue (MB) (Scheme 1). Remarkably, the adsorption of MB and MO can be completed in matter of minutes, compared to the slow kinetics reported so far in the literatures for HA-based adsorbents. Such polyalcohol-coated HA could lead to many more applications that demand as an efficient and low-cost adsorbent for water treatment application [17].

## 2. Experimental section

### 2.1. Materials

$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and D-Fructose-1,6-Phosphate trisodium salt octahydrate ( $\text{C}_6\text{H}_{11}\text{Na}_3\text{O}_{12}\text{P}_2 \cdot 8\text{H}_2\text{O}$ , DFP) were all purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. All the chemical reagents were analytical grade and used as received without further purification. Deionized (DI) water was used for rinsing and makeup of all aqueous solutions throughout the study.

### 2.2. Method

Typically, 3.9430 g  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and 2.06 g  $\text{C}_6\text{H}_{11}\text{Na}_3\text{O}_{12}\text{P}_2 \cdot 8\text{H}_2\text{O}$  were dissolved in 35 mL deionized water with 3 min ultrasonic treatment, respectively. Then the two solutions and 5 mL  $\text{NH}_4\text{OH}$  were mixed into a 100 mL Teflon autoclave, sealed and kept in an oven at 140 °C for 3 h. After self-cooling to ambient temperature, the product was collected by centrifugation, washed with deionized water 7 times and dried at 60 °C in air.

### 2.3. Characterization

X-ray powder diffraction (XRD) patterns were recorded using a

Rigaku D/max 2550 V X-ray diffractometer with a high-intensity Cu K $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). Fourier transform infrared (FT-IR) spectra were recorded on a spectrophotometer (Nicolet iS50, Thermofisher Scientific). Scanning electron microscopy (SEM) micrograph was performed on a field-emission scanning electron microscope (SU8000, Hitachi) at 5 kV. Transmission electron microscopy (TEM) image was obtained from a field-emission Transmission electron microscope (H-7700, Hitachi). UV–vis absorption spectra were taken on a spectrophotometer (UV-2600, SHIMAZDU). The Brunauer–Emmett–Teller (BET) specific surface area was measured by a surface area and pore size analyzer (BEL, Max). Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) with a heating rate of 10 °C/min from 30 to 1000 °C was conducted on a Netzsch Thermoanalyzer (STA 449).  $^{13}\text{C}$  cross polarization magic angle spinning (CPMAS) NMR spectra were recorded on a Bruker 400WB Avance III spectrometer ( $B_0 = 9.4 \text{ T}$ , Larmor frequency 400.13 MHz for  $^1\text{H}$ , 100.61 MHz for  $^{13}\text{C}$ ) with a 3.2 mm probe at room temperature. The MAS frequency was set to 10 kHz, the recycle delay was set to 5 s, and 8192 transients were accumulated by using a 90° pulse length of 2.29  $\mu\text{s}$  and 2 ms contact time.  $^{13}\text{C}$  chemical shifts were referenced to adamantane ( $\delta(\text{CH}_2) = 38.5 \text{ ppm}$ ).  $^{31}\text{P}$  CPMAS NMR spectra were performed on a Bruker 600WB Avance III spectrometer ( $B_0 = 14.1 \text{ T}$ , Larmor frequency 599.8 MHz for  $^1\text{H}$ , 242.8 MHz for  $^{31}\text{P}$ ). The MAS frequency was also set to 10 kHz, the recycle delay was set to 5 s, and 16 transients were accumulated by using a 90° pulse length of 2.80  $\mu\text{s}$  and 3.9 ms contact time.  $^{31}\text{P}$  chemical shifts were referenced directly to ammonium diphosphate (ADP) ( $\delta(\text{P}) = 0.81 \text{ ppm}$ ).

### 2.4. Bath adsorption experiments

Batch adsorption experiments were carried out by placing 25 mg as-prepared adsorbent into 200 mL of the corresponding dye solutions. The solutions were agitated with magnetic stirring at 600 rpm at room temperature. At each given contact time, 5 mL solution was extracted and centrifuged at 4000 rpm for 4 min, and then analyzed for dye concentration via a UV–vis spectrometer (Shimadzu, UV2600). The initial pH of the dye solutions was 6.70 as measured with a pH meter which approached the pH of the tap water. For measuring the effect of pH value on the dye adsorption, the dye solutions pH values were adjusted with HCl (1 N) or NaOH (1 N) solutions to the given values and the contact time was fixed as 20 min. The temperature effect experiments was carried out 25, 35 and 45 °C with an initial dye concentration of 50 ppm and a mass of HA of 25 mg in 50 mL solution, and the contact time was fixed as 20 min. The equilibrium adsorption capacity of the adsorbent for the dyes were calculated as follows:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where  $C_0$  (mg/L) and  $C_e$  (mg/L) are the initial and equilibrium

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