



Review

Tannic acid adsorption on amino-functionalized magnetic mesoporous silica

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ABSTRACT

Amino-functionalized magnetic mesoporous silica (magMCM-41-NH₂) was prepared and adsorption of organic pollutant tannic acid (TA) from aqueous solution on the resulting material was investigated. The adsorbent was characterized by elemental analysis, X-ray diffraction (XRD), transmission electron microscopy (TEM), N₂ adsorption-desorption, IR spectroscopy, Zeta potential measurements and vibration sample magnetometer (VSM). Characterization results showed that magMCM-41-NH₂ had ordered mesoporous structure with amino group content of 4.57 wt%, BET surface area of 668 m²/g and the pore volume of 0.525 cm³/g. Batch adsorption tests indicated that magMCM-41-NH₂ adsorbent exhibited high adsorption affinity towards aqueous TA with a maximum adsorption capacity of 510.2 mg/g. The Freundlich model could fit the adsorption isotherm of TA over magMCM-41-NH₂ very well, implying that adsorption process is heterogeneous. TA adsorption on magMCM-41-NH₂ could be well described by the pseudo-second-order kinetics. Adsorption of TA on the adsorbent was found to be strongly dependent on pH and ionic strength, suggesting that electrostatic interaction played a crucial role in TA adsorption. X-ray photoelectron spectroscopy (XPS) analysis confirmed the formation of complex compound between TA and surface amino groups of magMCM-41-NH₂ upon adsorption.

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1. Introduction

Phytic substances, such as tannic acid (TA) and gallic acid, are naturally occurring organic matters in surface and ground water, resulting from the decomposition of natural organic matter [1]. As a water soluble polyphenolic compounds, TA is considered to be toxic to aquatic organism, such as algae, fish and invertebrates. In particular, the presence of TA in drinking water may act as the precursor of carcinogenic disinfection byproducts (DBPs) [1–4]. Hence, minimization and removal of TA in water is of practical importance and interest.

A variety of treatment techniques have been developed to remove TA in water, including chemical oxidation, electrochemical method, coagulation, ultrafiltration, adsorption, and biological method [5–9]. Among them, the adsorption method has been intensively investigated. For example, zirconium pillared clay, chitosan, cationic surfactant-modified bentonite clay, resin, and activated carbon have been found to be effective for the adsorptive removal of aqueous TA [3,4,10,11]. However, the separation process of adsorbents from aqueous solution after saturated adsorption is usually complex and time-consuming.

Recently, magnetic mesoporous silica combining the advantage of mesoporous structure and sufficient magnetization has received great attention in environmental remediation. The magnetic mesoporous silica adsorbent has the unique large surface area, ordered mesoporous structure and narrow pore size distribution, which make it suitable candidate for pollutant adsorption in aqueous solution. Additionally, the magnetic mesoporous silica is susceptible to surface functionalization due to its abundant surface silanol groups. After saturated adsorption, moreover, magnetic mesoporous silica can be easily separated from mixture solution by external magnetic field. It should be emphasized that as an inert matrix mesoporous silica usually displays low adsorption capacity towards pollutants. Alternatively, surface functionalization of mesoporous silica by active amino group [12,13] or thio-group [14] may lead to markedly enhanced adsorption. Previous researches on magnetic mesoporous silica adsorbents mainly focused on the removal of aqueous heavy metal [15,16], and only a few studies have been conducted on adsorption of organic pollutants in water. For example, Tian et al. synthesized the magnetic hexagonal mesoporous which can remove DDT from aqueous solution [17]. Deng et al. prepared a superparamagnetic microsphere with an Fe₃O₄@SiO₂ core and mesoporous SiO₂ shell and observed fast removal of microcystins in water [18]. To our best knowledge, however, no study has been conducted on TA adsorption to surface functionalized magnetic mesoporous silica adsorbents thus far.

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In this study, magnetic mesoporous silica were prepared and further functionalized by aminopropyl group. The physical, chemical, and structural properties of the magnetic mesoporous silica were characterized by XRD, IR spectroscopy, elemental analysis, N₂ adsorption-desorption and Zeta potential measurement. The adsorption of aqueous TA on the synthesized adsorbent was evaluated by batch experiments and adsorption kinetic tests. The impacts of pH and ionic strength on TA adsorption were investigated. The mechanism of TA adsorption to the adsorbent was also proposed based on batch adsorption and XPS analysis results.

2. Materials and methods

2.1. Materials

TA and 3-aminopropyltrimethoxysilane supplied by Aldrich Chemical Co. were used as received without further purification.

2.2. Preparation of magnetic mesoporous silica

Magnetic MCM-41 was prepared by a two-step synthesis procedure as described by Chen et al. [19]. To prepare the magnetic Fe₃O₄ nanoparticles, 1.5 g of iron(III) chloride and 0.6 g iron(II) chloride were dissolved in 10 mL of deionized water purged by a N₂ flow (60 mL/min) for 0.5 h. The resulting mixture was then added under nitrogen to 50 mL solution of 1.0 mol L⁻¹ NH₃·H₂O solution containing 0.2 g of cetyltrimethylammonium bromide (CTABr) under sonication. After reaction for 30 min, the colloidal iron oxide nanoparticles were recovered magnetically. The magnetic MCM-41 sample was prepared by adding the as-synthesized Fe₃O₄ nanoparticles to 1.0 L solution containing 640 mL deionized water (degassed with nitrogen), 360 mL of 15 mol L⁻¹ NH₃·H₂O ammonia solution and 5.8 g CTABr under vigorous mechanical stirring and N₂ protection. After reaction for 30 min, 23.2 mL tetraethyl orthosilicate was added dropwise and the mixture further reacted at 30 °C for 24 h. The magnetic MCM-41 was magnetically collected. The organic template CTABr was removed by Soxhlet extraction with ethanol for 36 h followed by drying at 70 °C under vacuum for 12 h. The resulting material is referred to as magMCM-41.

The surface functionalized magMCM-41 was prepared by the post-grafting method. Briefly, 2.0 g of magMCM-41 particles was suspended in 100 mL of dry toluene containing 3.0 mL of 3-aminopropyltrimethoxysilane with mechanical stirring under N₂ protection. The mixture was refluxed at 110 °C for 12 h, then magnetically separated, followed by repeated washing by ethanol and drying at 70 °C under vacuum for 12 h. The amino-functionalized magMCM-41 is denoted as magMCM-41-NH₂. The Fe₃O₄ content in the composite material determined using the method described by Liu et al. [20] was 10.5 wt%.

2.3. Material characterization

Small angle X-ray diffraction (XRD) patterns of the samples were recorded on a powder diffraction-meter (D/max-RA, Rigaku), operating with a Cu anode at 40 kV and 40 mA in the range of 0.5–5° with a speed of 2 min⁻¹. Wide angle XRD patterns of the samples were measured in the range of 15–70°. Fourier transform-infrared (FT-IR) spectra were recorded in a FT-IR spectrometer (Nicolet 5700, Thermo Nicolet) at 2 cm⁻¹ resolution. N₂ adsorption-desorption isotherms were collected on a Micromeritics ASAP 2200 instrument. TEM observation was performed on a transmission electron microscope (H-800, Hitachi). Magnetic properties of the samples were measured by a vibration sample magnetometer (Lake Shore 7410, Lake Shore) under magnetic fields up to 10 kOe. The TGA curves were taken by using a thermo gravimetric analyzer (Pyris 1 TGA, PerkinElmer) under a stable N₂ flow. The temperature studied

ranged from 25 to 750 °C at a ramping rate of 20 °C/min⁻¹. Carbon, hydrogen and nitrogen contents of the samples were determined with elemental analyzer (CHN-O-Rapid, Heracus). X-ray photoelectron spectroscopy (XPS) measurement was conducted with a spectrometer (Escalab 250, Thermo-VG Scientific) with a Al KR X-ray source to determine the C, N, and O atoms present on the surface. All binding energies were referenced to the neutral C_{1s} peak at 284.6 eV to compensate for the surface charging effects. The Zeta potentials of the materials were determined according to reference [21].

2.4. Adsorption of TA

The batch experiments were carried out to evaluate TA adsorption isotherms over magMCM-41-NH₂. Typically, 10 mg of magMCM-41-NH₂ was added to 60 mL flask receiving 50 mL of TA solution with initial concentrations varying from 20 to 200 mg/L with pH 6.98–7.36. The flasks were transferred into an incubator, in which the tubes were shaken at 25 °C for 24 h. After reaching adsorption equilibrium, the adsorbent particles were magnetically separated from the aqueous solution and the residual concentrations of TA in the aliquot were determined using a UV-vis spectrometer with detecting wavelength at 278 nm [1]. The equilibrium adsorption amounts of TA were calculated according to Eq. (1):

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

where q_e is the amount of TA adsorbed at equilibrium, C_0 is the initial TA concentration, C_e is the equilibrium TA concentration, V is the volume of TA solution, and M is the adsorbent mass.

For adsorption kinetics at 25 °C, 100 mg of magMCM-41-NH₂ was fast introduced into a 500 mL three neck flask containing 500 mL of TA solution with an initial TA concentration of 50, 100, or 200 mg/L, respectively under strong mechanic stirring. 4 mL of solution was withdrawn at different time intervals. After magnetic separation of the adsorbent particles, the residual TA concentration was spectrophotometrically determined.

The pH effect on TA adsorption was investigated in a pH range from 3 to 10. A series of flasks containing 10 mg of magMCM-41-NH₂ and 50 mL of 100 mg/L TA solution with different pH pre-adjusted with 0.1 mol/L HCl or NaOH solution were shaken at 25 °C for 24 h. The residual TA concentrations were determined spectrophotometrically and adsorption amounts of TA were calculated according to Eq. (1).

Effect of background electrolyte on TA adsorption was studied by dispersing 10 mg of adsorbents in 50 mL NaCl, KCl or CaCl₂ solution (40–240 mg/L) containing 100 mg/L TA at pH 7.2.

3. Results and discussion

3.1. Material characterization

The crystalline structure of the magnetic nanoparticle was characterized using wide angle XRD and the result is shown in Fig. S1. The diffraction peaks with 2θ at 30.4°, 35.6°, 43.3°, 57.3°, and 62.8° were observed, indicative of a cubic spinel structure of the magnetite. The small angle XRD patterns of magMCM-41 and magMCM-41-NH₂ were compared in Fig. 1. For magMCM-41, three well-resolved diffraction peaks with 2θ at 2.22°, 3.88° and 4.42°, indexed to (100), (110) and (120) diffraction, were clearly observed, indicative of the presence of hexagonal mesoporous structure. The diffraction peaks are also visible in the XRD pattern of magMCM-41-NH₂, reflecting that the ordered hexagonal structure retained unchanged after aminopropyl group functionalization. Notably, the peak intensity of magMCM-41-NH₂ decreased

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