Removal of humic acid from aqueous solution by magnetically separable polyaniline: Adsorption behavior and mechanism

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Magnetically separable polyaniline ($Fe_3O_4@SiO_2$–PANI) was prepared by in situ chemical polymerization of aniline on the surface of silica-coated Fe_3O_4 nanoparticles, and characterized by FTIR spectroscopy, powder X-ray diffraction, elemental analysis, transmission electron microscopy, vibrating sample magnetometry and X-ray photoelectron spectroscopy. Characterization results showed that $Fe_3O_4@SiO_2$–PANI with amino groups of 1.78 mmol/g and the average diameter of 21.6 nm are superparamagnetic. Adsorption behavior of $Fe_3O_4@SiO_2$–PANI nanoparticles for humic acid (HA) was investigated by batch experiments and adsorption kinetic tests. HA adsorption amount on the adsorbent decreased with increasing solution pH and the presence of Ca^{2+} resulted in the enhanced HA adsorption. HA adsorption on $Fe_3O_4@SiO_2$–PANI could be well described by Langmuir model and the maximum adsorption amount of the adsorbent for HA at 25 °C was 36.36 mg/g. HA adsorption process on the adsorbent obey pseudo-second-order kinetics and the adsorption rates decrease with increasing initial HA concentration. The XPS analysis verified that HA adsorption over the adsorbent could be attributed to the surface complexation between the disassociated HA molecules and the protonated nitrogen of polyaniline on the adsorbent. HA loaded adsorbent could be magnetically separated and easily desorbed in 0.01 mol/L NaOH solution. Regeneration tests indicated that $Fe_3O_4@SiO_2$–PANI could be used repeatedly.

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1. Introduction

Humic acid (HA), the major constituent of dissolved organic matter, was ubiquitously present in natural water as a result of the decomposition of plant, animals and other biological activities of microorganisms in natural systems. The presence of HA in natural waters may cause an undesirable color and taste, and serve as a nutrient for bacterial growth in water distribution system. It may lead to membrane fouled during various membrane processes, which increases the cost of membrane treatment. Moreover, HA molecules may bind with the aqueous heavy metals, pesticides, and herbicides, to yield high concentrations of these substances. More importantly, HA can be interacted with chlorine disinfectants during the drinking water production to form carcinogenic chlorinated organic compounds [1,2]. Therefore, the minimization of the HA presence in drinking water is of great importance.

Various processes such as chemical coagulation, advanced oxidation, membrane separation, adsorption, biodegradation and so on, have been studied to remove HA from the aqueous solution. Among these, adsorption technique has been considered as an effective one due to it is simplicity, high efficiency and ease operation. Numerous attempts have been made to develop suitable adsorbent for the removal of aqueous HA [3–7]. Aminated adsorbents such as chitosan [8–10], polypyrrole [11], aminated polyacrylonitrile fibers [12], amino-functionalized mesoporous silica [13,14] and amine-modified polyacrylamide–bentonite composite [15] and so on, have been applied to eliminate aqueous HA because of their strong affinity for aqueous HA. The enhanced HA adsorption on the aminated adsorbents may be attributed to the strong electrostatic interaction between the positively charged adsorbents and negatively charged HA. In our previous study, polyaniline (PANI) and it is composites with large amount of amine and imine nitrogen have also exhibited high adsorption capacity for the aqueous HA [16,17]. However, the associated adsorption mechanism of HA on the PANI based adsorbents has not yet been clarified. In addition, the separation and recovery of the saturated PANI based adsorbents are very difficulty, which limits the application of

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these adsorbents. In recent years, magnetic separation technology as a promising alternative method to solve the problem of separation and recovery of conventional powdery adsorbents, has received great attention [18–20]. For example, the magnetic chitosan [21], amine functionalized magnetic mesoporous composite microspheres [13], magnetic polyacrylic anion exchange resin [22] and so on, have been used as adsorbents for the removal of humic acid in aqueous solution. However, to our best knowledge, no efforts have been made to eliminate the aqueous HA by magnetically separable PANI adsorbent.

The most common magnetic adsorbents are assisted on iron oxides, which are easily oxidized and eroded in aqueous solution. Due to the chemical stability and ease of subsequent functionalization of SiO_2, silica has frequently used as an ideal coating layer to protect the magnetic core, for example, magnetic EDTA-modified chitosan/SiO_2/Fe_3O_4 [23], Fe_3O_4/SiO_2 core/shell nanoparticles attached to graphene oxide [24], thiol modified Fe_3O_4@SiO_2 [25], amino-functionalized Fe_3O_4@SiO_2 [17] and so on, have been developed as an adsorbent for removal of aqueous pollutants. Therefore, silica-coated Fe_3O_4 (Fe_3O_4@SiO_2) nanoparticles were synthesized as a magnetic core, and magnetic PANI adsorbent (Fe_3O_4@SiO_2–PANI) was prepared by in situ chemical oxidation of aniline on the surface of Fe_3O_4@SiO_2 nanoparticles. The adsorbent was characterized by Fourier transform infrared (FTIR), powder X-ray diffraction (XRD), elemental analysis, transmission electron microscopy (TEM), vibrating sample magnetometry (VSM) and X-ray photoelectron spectrometry (XPS). The adsorption and desorption behaviors of HA in aqueous solution on the adsorbent were studied. The associated adsorption mechanism was also proposed.

2. Materials and methods

2.1. Materials

HA of ACS reagent grade was supplied by Aldrich Chemical Co. All other reagents of analytical grade were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China.

2.2. Adsorbent preparation

Magnetic PANI adsorbent was prepared by a three-step synthesis procedure. First, Fe_3O_4 nanoparticles were synthesized by chemical precipitation. Typically, 0.04 mol iron(III) chloride and 0.02 mol iron(II) chloride were dissolved in 50 ml of 0.5 mol/L HCl solution. The resulting mixture was added dropwise to 500 ml of 1.5 mol/L NaOH at 80 °C under a nitrogen flow (40 ml/min) with vigorous stirring. The black Fe_3O_4 nanoparticles were separated magnetically and washed repeatedly with deionized water followed by drying at 50 °C under vacuum for 4 h.

Second, 0.5 g Fe_3O_4 nanoparticles were washed by 0.1 mol/L HCl, then suspended in the mixture of 240 ml ethanol and 60 ml deionized water. After sonicated for 30 min at 25 °C, the $NH_3·H_2O$ was added to the mixture until the pH was adjusted to 11.0. Then, 1 ml TEOS was added dropwise to the mixture and stirred mechanically for 12 h. The resulting Fe_3O_4@SiO_2 nanoparticles were separated magnetically and washed several times with deionized water, followed by drying at 50 °C under vacuum for 12 h.

Third, the magnetic PANI was prepared by in situ chemical oxidation of PANI on the surface of Fe_3O_4@SiO_2. Detailly, 0.3 g Fe_3O_4@SiO_2 was suspended in 50 ml deionized water and sonicated for 30 min at room temperature. Then, 0.2 ml aniline was added into the suspension and the pH was adjusted to 3.0 by 1 mol/L HCl. After stirred for 1 h, ammonium persulfate solution (0.26 g ammonium persulfate dissolved in 2 ml deionized water) was added dropwise to the suspension. The reaction mixture was then stirred in ice bath for 6 h. The solid was collected by magnetic separation and thoroughly washed by deionized water, followed by drying at 50 °C under vacuum for 12 h. The materials obtained are referred to as Fe_3O_4@SiO_2–PANI.

2.3. Equipments and methods of characterization

The FTIR spectra of three nanoparticles were recorded on a Nicolet Nexus 870 FTIR spectrometer (Nicolet, USA) with the KBr pellet technique. The XRD data were collected with a Shimadzu XRD-6000 X-ray diffractometer using Cu Ka radiation. Carbon, hydrogen, and nitrogen contents were measured by a Heraeus CHN-O-Rapid elemental analyzer (Heraeus, Germany). The TEM observations were collected on a Hitachi H-800 transmission electron microscope (Hitachi, Japan). The magnetic property of three nanoparticles was determined using a VSM (VSM 7410, Lake Shore, USA). X-ray photoelectron spectroscopy (XPS) analysis of Fe_3O_4@SiO_2–PANI before and after HA adsorption was conducted on a VG ESCALB MK-II Instrument (VG, UK). The high-resolution spectra of N1s and C1s were fitted by XPSpeak 4.1 software. Zeta potentials of Fe_3O_4@SiO_2–PANI after HA adsorption in absence and presence of Ca^{2+} were measured using a Zeta Potential Analyzer (Zeta PALS, Brookhaven Instruments Co., USA).

2.4. Adsorption tests

Adsorption isotherms of HA on Fe_3O_4@SiO_2–PANI were evaluated by placing 20 mg of adsorbent in 50 ml polytetrafluoroethylene-lined screw cap glass tubes containing 40 ml of HA with initial HA concentration from 4.65 to 51.15 mg/L at pH 5.5–6.0. The suspensions were shaken for 24 h at 120 rpm and 15, 25 and 35 °C, respectively. Then, the solutions were separated magnetically and the residual concentrations of HA were determined by a UV–vis spectrometer with detecting wavelength at 254 nm. The adsorption amounts of HA on the adsorbent were calculated by the mass balance of HA in solutions before and after adsorption.

Adsorption kinetic experiments were performed by dispensing 200 mg Fe_3O_4@SiO_2–PANI in 500 ml flask receiving 400 ml of HA with initial concentration of 14.06, 28.13 and 41.85 mg/L, respectively. The mixture was stirred with 800 rpm at 25 °C. At predetermined time intervals, 4 ml of the mixture was withdrawn and separated magnetically for the analysis of residual HA concentration.

The effect of solution pH on HA adsorption over Fe_3O_4@SiO_2–PANI nanoparticles was studied by placing 20 mg of adsorbent in 40 ml of HA solution with concentration of 27.90 mg/L and the pH values were adjusted from 2 to 10 with 0.1 mol/L HCl or NaOH solution. The effect of inorganic cations on the adsorption process was determined by mixing 20 mg of adsorbent with 40 ml Na^+, Ca^{2+} (1.25–15 mmol/L) solution containing 27.90 mg/L HA at pH 6.0.

2.5. Desorption experiments

Based on the experiments of pH effect on HA adsorption over the adsorbent, 0.01 mol/L NaOH was used as a desorption agent. Eighty milligram of Fe_3O_4@SiO_2–PANI was dispersed in 111.71 mg/L of HA solution. The HA-loaded adsorbent was separated magnetically. After washing several times with ionized water to remove the unadsorbed HA, HA-loaded adsorbent was suspended in 30 ml 0.01 mol/L NaOH and shaken at 25 °C for 12 h. The regenerated adsorbent was again used for further adsorption of HA. Adsorption of HA and regeneration of HA-loaded adsorbent was conducted with five consecutive cycles.