

An effective approach for fast selective separation of Cr(VI) from water by ion-imprinted polymer grafted on the electro-spun nanofibrous mat of functionalized polyacrylonitrile

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ABSTRACT

The aim of this study is to prepare Cr(VI) ion-imprinted polymer (IIP) grafted on the surface of functionalized polyacrylonitrile nanofibrous mat (FPANFM), IIP-functionalized-PANFM, for the removal of Cr(VI) from aqueous solutions. The prepared materials were characterized by FT-IR, TGA, FESEM, and energy dispersive X-ray spectroscopy (EDS). Moreover, various operating conditions such as contact time, initial metal ion concentration (5–500 mg L⁻¹), IIP-functionalized-PANFM dosage and FPANFM/IIP weight ratio. The imprinting efficiency was evaluated by comparing the adsorbed amount of Cr(VI) by IIP and IIP-functionalized-PANFM with the adsorption by the non-imprinted polymer (NIP). Cr(III), Cu(II), and Cd(II) were selected as interferences and used individually to study the selectivity factor. The maximum adsorption capacity was < 30 mg g⁻¹ for NIP, PANFM, and FPANFM, while for IIP and IIP-functionalized-PANFM was 183 mg g⁻¹ and 398 mg g⁻¹ in a very short time (12 min.), respectively. Moreover, the reusability of the IIP and IIP-functionalized-PANFM was tested for several times and no significant loss in adsorption capacity was observed. Also, isotherm models, kinetic adsorption mechanism and thermodynamic parameters were investigated.

1. Introduction

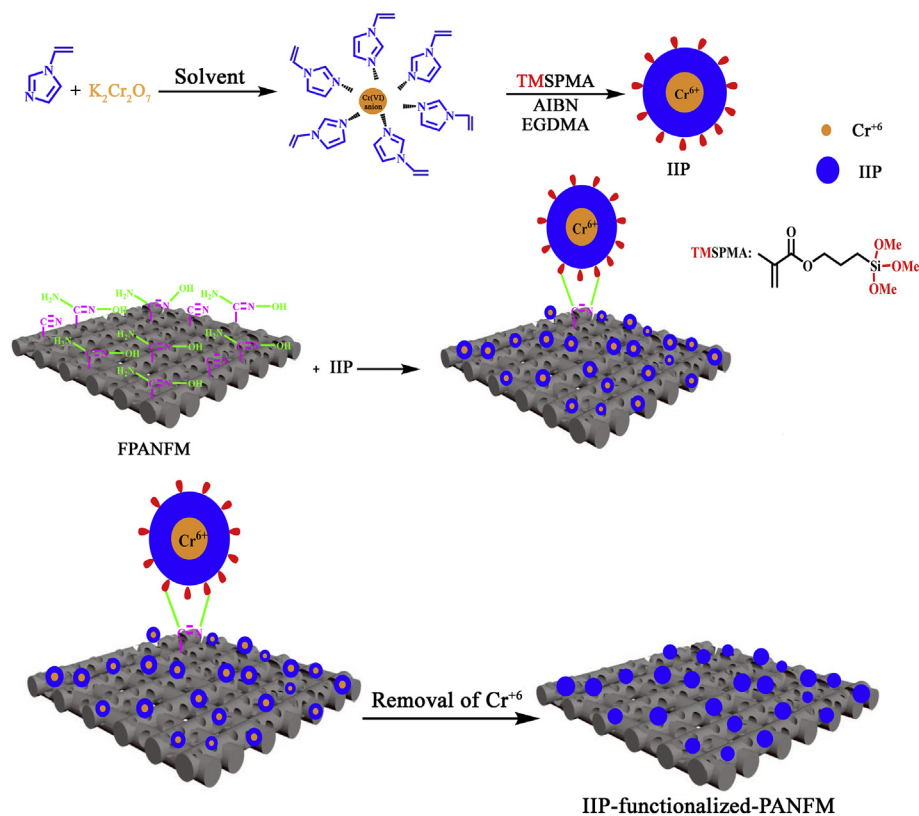
Serious pollution problems have been produced by worldwide industrial activities because of the release of the highly toxic organic and heavy metals in the rivers [1]. Industrial processes such as plating, tanning, paint production, pigment production and metallurgy involve the use of Cr(VI) compounds and are therefore the most frequent source of hexavalent chromium [2]. While Cr(III) is one of the main chemical form found in foods and is essential for maintaining normal glucose metabolism [2] Cr(VI) ions are non-biodegradable and highly toxic [3, 4], and may be involved in the pathogenesis of some diseases like liver, kidney, lung and gastrointestinal cancers. Therefore, Cr(VI) should be eliminated from used waters before disposal. Among various methods for the removal of heavy metal ions and organic pollutants from water such as chemical precipitation [5], electrochemical treatment [6], ion exchange [7], membrane separation [8], liquid extraction [9], and reverse osmosis [10], separation with molecularly imprinted polymers (MIPs) with particular functional groups are an attractive method and have been used by researchers [11, 12].

The MIPs possess several advantages such as good mechanical/chemical stability, ease of preparation, possible reusability, good

physical and chemical stability in different experimental conditions, and low fabricating cost. In preparation of MIPs, a molecular template acts as a mold and directs the positioning of the functional monomers around the template molecule which are then copolymerized with a cross-linker leading to the formation of template matching binding sites [13]. Ion-imprinted polymers retain all virtues of MIP, except that they recognize metal ions after imprinting [14, 15]. Selection of a polymeric adsorbent in a MIP system depends on the several factors such as size and coordination number of the ions, charges, and the coordination geometry [16]. The use of MIPs and membranes for the isolation and removal of contaminants has many advantages and are usual for separations [17, 18]. Porous fiber ultrafiltration membranes are widely used for separations and removal of pollutants from water/wastewater in industrial and non-industrial applications, and also as a reverse osmosis pretreatment [19, 20]. Polyacrylonitrile (PAN) with characteristics such as good thermal stability, excellent solvent resistance, high mechanical strength, and resistance to bacteria and photo-irradiation has been used successfully in the production of membranes [21, 22]. Different functional materials can be made by using particular reactions with the nitrile (–C≡N) groups in PAN [23, 24]. Amidoxime PAN nanofibrous mats could be prepared by treating PAN nanofibrous mats in

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Scheme 1. Illustration of synthesis procedure of IIP-functionalized-PANFM.

hydroxylamine hydrochloride aqueous solution. Conversion of nitrile groups to the hydrophilic amidoxime groups improves the chemical and biological properties of PAN and has been widely used in the environmental and biological applications [25, 26]. Therefore, because of the water shortages and increasing environmental pollution, novel strategies are highly promising for the removal of heavy metal ions such as Cr(VI) from polluted waters.

To our knowledge, grafting IIP particles on the surface of porous PAN nanofibers mat is new and has not been reported before. In this study, we expect that the combination of IIP and amidoxime-functionalized PAN nanofibers mat (IIP-functionalized-PANFM) provide effective synergism for the adsorption of Cr(VI) in the aqueous solutions. Therefore, the novel Cr(VI) adsorbent (IIP-functionalized-PANFM) is fabricated by grafting the prepared IIP particles on the surface of amidoxime-functionalized PAN nanofibers mat (FPANFM). The IIP is synthesized via free radical polymerization using mixture of 1-vinylimidazole (1-VI) and 3-(Trimethoxysilyl)propyl methacrylate (TMSPMA) as the functional monomer and co-monomer, ethylene glycol dimethacrylate (EGDMA) as cross-linker, and *N,N*-azobisisobutyronitrile (AIBN) as initiator in the presence of $Cr_2O_7^{2-}$ as the target template. Porous PAN fiber mat is prepared by electrospinning PAN in DMF solution with poly(methyl methacrylate) (PMMA) as the pore-forming agent, and then functionalized with amidoxime groups via reaction of the nitrile groups with hydroxylamine hydrochloride. The prepared materials are characterized by FT-IR, TGA, FESEM, and EDS. The adsorption characteristics of IIP and IIP-functionalized-PANFM for Cr(VI) in aqueous solutions are investigated at various experimental conditions and the selectivity is checked in the presence of Cr(III), Cu(II), and Cd(II) as interferences. The adsorption kinetics, isotherms, and regeneration of the adsorbents (IIP and IIP-functionalized-PANFM) are also investigated.

2. Materials and methods

2.1. Reagents

1-vinylimidazole (1-VI) and 3-(trimethoxysilyl)propyl methacrylate (TMSPMA) as organic functional monomer and co-monomer, respectively, ethylene glycol dimethacrylate (EGDMA) as crosslinking agent, and *N,N*-azobisisobutyronitrile (AIBN) as initiator, sodium carbonate, hydroxylamine hydrochloride, dimethylformamide (DMF) and poly(methyl methacrylate) (PMMA, $M_w = 120,000 \text{ g mol}^{-1}$) were obtained from Sigma-Aldrich (Steinheim, Germany). Polyacrylonitrile (PAN, $M_w = 150,000 \text{ g mol}^{-1}$) was supplied by Polyacryle Co. Esfahan, Iran. Acetone, ethanol, potassium dichromate ($K_2Cr_2O_7$), sodium hydroxide (NaOH), copper (II) chloride ($CuCl_2$), cadmium (II) chloride ($CdCl_2$), chromium (III) chloride ($CrCl_3$), and other chemicals were all of the analytical grades. All the chemicals were of reagent grade and used without any further purification.

2.2. Instrumentation and characterizations

Fourier transform infrared (FT-IR) spectra of the nanoparticles were recorded with Bruker Tensor 27 spectrometer using KBr method. Thermogravimetric analysis (TGA) was performed by a DuPont Instruments TGA 951 from room temperature to 700°C with a heating rate of $10^\circ\text{C min}^{-1}$ in a nitrogen flow. The products sizes were characterized by Field emission scanning electron micrographs (FESEM) using a Mighty-8 instrument (TSCAN Company, Prague). Scanning electron microscopy–energy dispersive spectroscopy (SEM–EDX) analyses were carried out using Mighty-8 instrument (TSCAN Company, Prague). A Perkin-Elmer Analyst 900 atomic absorption spectrometry with deuterium background corrector and equipped with a chromium hollow cathode lamp operated at 25 mA was used. The wavelength and spectral band pass were set at 357.9 nm and 0.7 nm, respectively. A 10 cm long slot-burner head and an air–acetylene flame were used. An

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