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Selective recognition of molybdenum(VI) from water by Mo(VI) oxy ion-imprinted particle as an adsorbent

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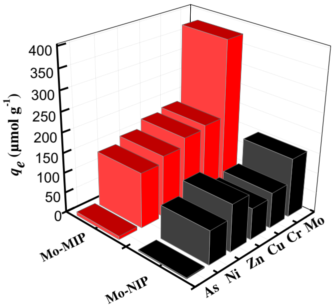
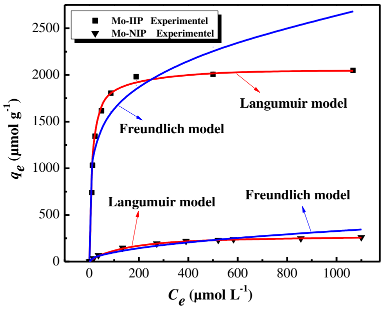
HIGHLIGHTS

- ▶ Mo-IIP by the surface metal ion imprinting technique with a sol–gel process.
- ▶ Isonicotinic acid as a functional monomer firstly.
- ▶ The saturate binding capacity of Mo-IIP is 2171.46 μmol g^{-1}.
- ▶ Mo-IIP shows an efficient selectivity towards imprinted Mo(VI) in water phase.

GRAPHICAL ABSTRACT





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ABSTRACT

The isonicotinic acid (4-picolinic acid) served as a functional monomer firstly to prepare Mo(VI) oxy ion-imprinted particle (Mo-IIP) by the surface metal ion imprinting technique with a sol–gel process on the surface of amino-silica, and TEOS acted as a cross-linker monomer. The prepared Mo-IIP was characterized and its proper selectivity recognition ability was investigated by single binding experiments comparing to Mo(VI) oxy ion non-imprinted particle (Mo-NIP). Furthermore, the reuse was carried out. A possible imprinting mechanism was put forward for the Mo-IIP. The binding process fitted well to the pseudo-second-order kinetic model, the Langmuir model, and the Weber–Morris model. The results suggested that a multi-step with the film and intraparticle diffusion process might dominate this chemical sorption for Mo(VI) binding onto Mo-IIP. The Mo-IIP exhibited selectivity for Mo(VI) with a remarkably high binding capacity 2171.46 μmol g^{-1}, which was 7.6 times higher than that of the Mo-NIP. Such

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efficient selectivity might be due to the complexation ability of nitrogen atom in the 4-picolinic acid with supper memory sites after imprinting process. The excellent affinity and exclusive selectivity make the Mo-IIP become an potential material for Mo(VI) removal and concentration from the water environment.

1. Introduction

Molybdenum is a refractory metallic element, which is widely used in electron tubes, vacuum tubes, heat-resistant materials, and high-strength steel alloys [1]. It is an essential trace element for both animals and plants, but has long been known as one of the biologically active transition elements in the environment [2]. Water soluble molybdate anions cause an environmental problem if their concentration exceeds 5 ppm [3]. Special attention should be given to Mo(VI) due to its toxicity and the negative effects on flora and fauna [4]. Therefore, it is necessary to separate or concentrate the oxy Mo(VI) from the water environment. Many new separation methods have been focused on, such as electrochemical removal, biological treatment, adsorption procedure, membrane and ion exchange [5]. Among all, adsorption is recognized as an effective and economic method for the removal of trace metals from the wastewater. Many adsorbents have been studied from aqueous solutions, including carbon cloth [6], goethite [7], ferric oxide gel [8], γ-Al_2O_3 [9], natrolite [10], pyrite [11], and carminic acid modified anion exchanger [12] etc. However, new adsorbents for Mo(VI) with highly selective adsorption capacity and fast adsorption–desorption kinetics from the water are in great demand.

Molecular imprinted polymer (MIP) is a new smart material, which has remarkable recognition properties for its template [13]. Metal ion imprinted polymers (MIIPs) are based on MIP technique; they recognize metal ions after imprinting and retain all virtues of the imprinting technology [14]. MIIP has developed rapidly in removing or detecting toxic heavy metal ions owning to its good selectivity [15–17]. However, most previous MIIPs were prepared by the polymerization of suspension, polymerization, bulk, dispersion and emulsion [18,19]. It is deserved to notice that all those imprinting materials were synthesized in organic phase with the problems of hard conditions and complex processes, even though they have a good combination property for absorbing metal ions [20]. Recently, more and more technique are focus on the surface metal ion imprinted materials with a sol–gel process [21,22], the supports of the surface imprinted materials are silica nanoparticles, which are mechanical/chemical stability, low cost, ease of preparation, and the targets are easier to remove [23]. In our previous work, we have prepared BPA-imprinted polymers on the surface of silica microparticles with a molecular imprinting technique in a sol–gel process; it had the characteristics of high sorption capacity and fast and selective binding for BPA [24]. In this study, we try to prepare the metal ion imprinting polymer with high selectivity by a sol–gel process, as the nature of the functional monomer has a strong influence on the selective binding characters; the key factor is to find a suitable functional monomer for the metal imprinting process. It was reported that 4-vinylpyridine [25,26], 2-vinylpyridine [22], acrylamide [27], porous polyvinylidene fluoride [28] and 2, 2′-dipyridine [29] could be used as functional monomer in the imprinting process. Therefore, the above functional monomer used in the metal ion imprinted polymer excited interest to us, it seemed that the pyridine groups had a great affect on the metal ion sites in the imprinting process. Consequently, isonicotinic acid (4-picolinic acid), a structurally related analog, which was an environment friendly and harmless, was employed as an alternative functional monomer in our work.

In this study, we presented a surface metal ion imprinted technique to prepare Mo(VI) oxy ion imprinted particle (Mo-IIP). Isonicotinic acid was firstly selected as a functional monomer in a sol–gel process with binding sites situated at the surface of the amino-silica gel. A possible mechanism was proposed on how the metal ions were imprinted onto Mo-IIP. The characters of Mo-IIP were denoted by scanning electron microscopy (SEM), energy dispersive spectrometer (EDS), a standard Brunauer–Emett–Teller (BET) analysis, Fourier transform infrared spectrometer (FTIR) and thermogravimetric analysis (TGA) in detail. The virtue of Mo-IIP and Mo-NIP were estimated by the binding kinetics and isotherms. The selective recognition of oxy Mo(VI) was evaluated by static binding tests. And the reuse performance was tested for six times. Mo-IIP developed in this work can serve as an efficient selective material for enriching and determining Mo(VI) from water environment. All these discussions will be beneficial to further improvement and may be a theoretical direction for its potential application in practice.

2. Experimental

2.1. Materials and chemicals

Tetraethyl orthosilicate (TEOS), isonicotinic acid (4-picolinic acid), alcohol, $Na_2MoO_4 \cdot 2H_2O$, methanol, ammonia, (3-aminopropyl) triethoxysilane (APTES), acetic acid (AcOH) and all other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. (Taijin, China). All the chemicals used were of analytical grade. The solution used in this work was prepared by deionized water.

2.2. Instrumentations

The surface micrograph and element distribution of the prepared samples were characterized by a S4800HSD scanning electron microscope (Japan) and an H-7650 transmission electron microscopy (Japan). FTIR spectra were recorded using an AVATAR 360 FTIR spectrometer (USA) with a spectral range of 4000–400 cm^{-1}. The surface area and the pore parameters were analyzed by an ASAP 2020 multipoint Brunauer–Emett–Teller apparatus (USA). Thermogravimetric analysis was performed by a NETZSCH STA 409 PC/PG (China). ICPS-750 (Perkin Elmer) was used for detecting the concentration of Mo(VI) in the water.

2.3. Preparation of samples

The uniform silica nanoparticles were synthesized by TEOS hydrolysis with ammonium hydroxide according to the report by Stöber [30]. The prepared nano-silica (dry weight) was dispersed for 20 min in the carbinol solution by the ultrasound. Then the mixture of nano-silica, APTES, TEOS and acetic acid (1.0 mol/L) were stirred for 18 h at room temperature after adding in sequence. The resulted amino-silica was finally washed with anhydrous ethanol and dried at 80 °C for 12 h. Mo-IIP was prepared by the surface metal ions imprinting technique with a sol–gel method. Firstly, the amino-silica was dispersed homogeneously in 50 mL ethanol solution (50% v/v) by ultrasonic dispersion for 20 min to form suspension A, and 0.123 g isonicotinic acid and 0.484 g $Na_2MoO_4 \cdot 2H_2O$ were dissolved in 100 mL