



Development of an anion imprinted polymer for high and selective removal of arsenite from wastewater

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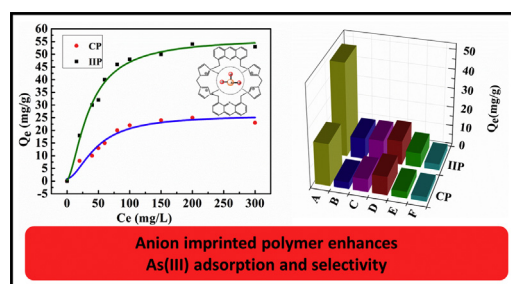
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HIGHLIGHTS

- As(III)-ion imprinted polymer (As-IIP) developed for selective As(III) adsorption.
- As-IIP has a maximum As(III) adsorption capacity of 55 mg/g at pH 8.
- Langmuir adsorption isotherms suggest monolayer As(III) adsorption.
- As(III) adsorption on As-IIP followed pseudo-second-order kinetics.
- 9.8% decrease of As-IIP adsorption capacity after five adsorption-desorption cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel cyclic functional monomer (CFM) was used to develop an As(III)-ion imprinted polymer (As-IIP). CFM possesses a positively charged imidazolium moiety and its specific cyclic size matches that of As(III). Batch adsorption experiments showed that the As-IIP has a maximum As(III) adsorption capacity of 55 mg/g, while that of the control polymer (CP) is only 25 mg As(III)/g. Adsorption isotherms for As(III) agree with the Langmuir model, suggesting monolayer adsorption. Kinetic studies showed that the adsorption process followed pseudo-second-order kinetics. The relative selectivity coefficients of As-IIP compared to CP for $\text{Cl}^-/\text{H}_2\text{AsO}_3^-$, $\text{SO}_4^{2-}/\text{H}_2\text{AsO}_3^-$, $\text{HPO}_4^{2-}/\text{H}_2\text{AsO}_3^-$, $\text{NO}_3^-/\text{H}_2\text{AsO}_3^-$, and $\text{Mo}_7\text{O}_{24}^{6-}/\text{H}_2\text{AsO}_3^-$ are 1.03, 1.95, 2.55, 1.52 and 2.51, respectively. The removal efficiency of As-IIP for As(III) in actual industrial wastewater was nearly 100%, which confirms that As-IIP has a high adsorption capacity as well as selectivity for the removal of As(III) from wastewater.

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1. Introduction

Water pollution by toxic heavy metals is becoming an increasingly significant issue of environmental concern world-wide (Islam et al., 2015; Li et al., 2018; Zou et al., 2016; Yu et al., 2018). Arsenic is one of the most toxic heavy metals that seriously threatens human and environmental health (Durube et al., 2007; Järup, 2003). In particular, As

(III) is more toxic and mobile than As(V) (Li et al., 2012). Uptake of even trace amounts of As(III) compounds can be fatal. The World Health Organization (2008) has set a maximum contaminant level for As in drinking water at 10 µg/L. Numerous methods for the removal of As from water exist, such as oxidation, precipitation, coagulation, membrane separation and adsorption (Cheng et al., 2016; Mohan and Pittman Jr, 2007; Song et al., 2018; Wen et al., 2017). Among these methods, adsorption is more attractive because of low cost, simple design and ease of operation, especially for a high removal efficiency from dilute aqueous solutions. Various materials, such as magnetite-

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reduced graphene oxide (Chandra et al., 2010), laterite (Glocheux et al., 2013) and cryogels (Kumar et al., 2013) have been investigated for the adsorption of arsenic. Although several studies have indicated that the above-mentioned adsorbents can remove As(III), the selectivity of these adsorbents was not studied. Therefore, it is imperative to develop an adsorbent which is highly selective and has a high capacity to completely remove As(III) from aqueous solutions.

Ion imprinted polymers (IIPs) have an incomparable advantage in selective adsorption and recovery of heavy metals because of their unique cavity structure and specific adsorption sites, complementary to the target ions (Fu et al., 2015; Rao et al., 2006). Thus, IIPs promise to be a new generation of novel adsorbents, which can also be regenerated chemically and recycled, which further lowers the treatment cost. Different kinds of imprinted polymer adsorbents have been synthesized and applied for the selective removal of heavy metal cations, such as Cu (Hoai et al., 2010), Cd (Zhu et al., 2017), Ni (Saraji and Yousefi, 2009), and Pb (Liu et al., 2011). However, arsenic species in natural waters generally exist as oxyanions (H_2AsO_3^- , HAsO_3^{2-}) rather than as metal cations. Compared with metal cations, the ratios of the charge to the radius of metal anions are lower 3–5 times (Alizadeh et al., 2016), which significantly reduces the electrostatic effect with functional monomers or ligands; thus, their specific recognition sites are difficult to form. Secondly, anions do not easily dissolve in nonpolar agents usually used in the imprinting process (Vilar, 2008). For the above-mentioned two reasons, metal anions are seldom considered as templates in ion imprinting. Therefore, it is a challenging task to design anion-imprinted polymers.

The choice of an appropriate functional monomer or ligand is crucial for the preparation of high performance anion imprinted sorbents. Charged H-bond interactions of anions occur with amide, pyrrole, urea, ammonium, and guanidinium groups through the $\text{N}\cdots\text{H}\cdots\text{A}$ interaction such as in 2-vinyl pyridine, 4-vinyl pyridine, and 1-vinyl imidazole (Yousuf et al., 2014). In addition, compounds with a macrocyclic structure can be used to recognize anions with large ionic radius through the appropriate size and the chelation ability of the ring, which possesses a variety of chemical functional groups. In our previous work, macrocyclic compounds, such 2-(allyloxy) methyl-12-crown-4 (Luo et al., 2015b), and 4-vinylbenzo-18-crown-6 (Luo et al., 2013), were functional monomers used to develop a lithium ion-imprinted polymer and a Pb(II) ion-imprinted polymer, respectively. In the above two cases, the so called “macroscopic effect” was utilized. The “macroscopic effect” refers to the ability of cyclic compounds to selectively recognize target molecules or ions due to the appropriate ring size matching with target molecules or ions.

For the work reported here, a novel cyclic functional monomer (CFM) with a positively charged moiety, tetra bromine-bi-4, 5-2(methylene bi-imidazole) acridine, was synthesized and used to prepare an As(III)-ion imprinted polymer (As-IIP). We investigated the size matching and electrostatic dual-effects on the performance of As-IIP. We found that As-IIP exhibits preferential binding and very high selectivity for As(III). The results of X-ray photoelectron spectroscopic (XPS) analysis verified that the CFM plays a major role in As(III) adsorption. In regeneration and actual application experiments, As-IIP showed good reusability and a high removal efficiency for As(III) from an actual industrial wastewater. Thus, the As-IIP adsorbent is a promising polymer for the efficient and selective removal of As(III) from aqueous solutions.

2. Materials and methods

2.1. Chemicals

Chemicals used in this study are listed in Text S1 (Supplementary Material). All chemicals were of analytical reagent grade. Water was purified through a Milli-Q water system (Bedford, USA).

2.2. Synthesis of cyclic functional monomer (CFM) and preparation of As(III)-ion imprinted polymer (As-IIP) and control polymer (CP)

Details on the synthesis and characterization of CFM are provided in the Supplementary Material (Text S2).

In the first step, 0.25 g functional monomer and 0.065 g NaAsO_2 were dissolved in 10 mL dimethyl sulfoxide and purged with nitrogen gas for 10 min. Then, the mixture was stirred for 1 h at 60 °C. In the second step, 0.5 mL of ethylene glycol dimethyl acrylate (EGDMA) and 30 mg of 2,2-azobisisobutyronitrile (AIBN) were added to 10 mL methanol and ultrasonically mixed for 5 min. The suspension was added to the mixed solution of the first step, the temperature raised to 70 °C, and the reaction mixture was stirred with reflux condensation for 12 h. The resultant polymer was separated by centrifugation at 8000 rpm for 5 min and then washed three times with methanol. Then, the particles were washed with 0.5 M sodium hydroxide repetitiously to remove the AsO_2^- until the filtrate did not contain AsO_2^- , followed by thorough washing with distilled water until a pH of 7 was reached. The CP was prepared and purified under identical conditions, except that the functional monomer was omitted.

2.3. Characterization of polymeric adsorbents

The morphology of the adsorbents was examined using a SSX-550 scanning electron microscope (SEM, Shimadzu, Japan). Thermogravimetric analysis (TGA) was carried out using a TGA Q600 SDT thermogravimetric analyzer (New Castle, USA). X-ray photoelectron spectroscopy (XPS) measurements were taken with a VG Escalab 250 spectrometer equipped with an Al anode ($\text{Al} - \text{K}\alpha = 1486.7 \text{ eV}$). The zeta potential of the adsorbent was measured with a Malvern zetasizer Nano ZS (Malvern Instruments, UK). The specific surface area (Brunauer–Emmett–Teller, BET) of the samples was measured using a F-Sorb 3400 automatic surface area from Gold APP Instrument (Beijing,

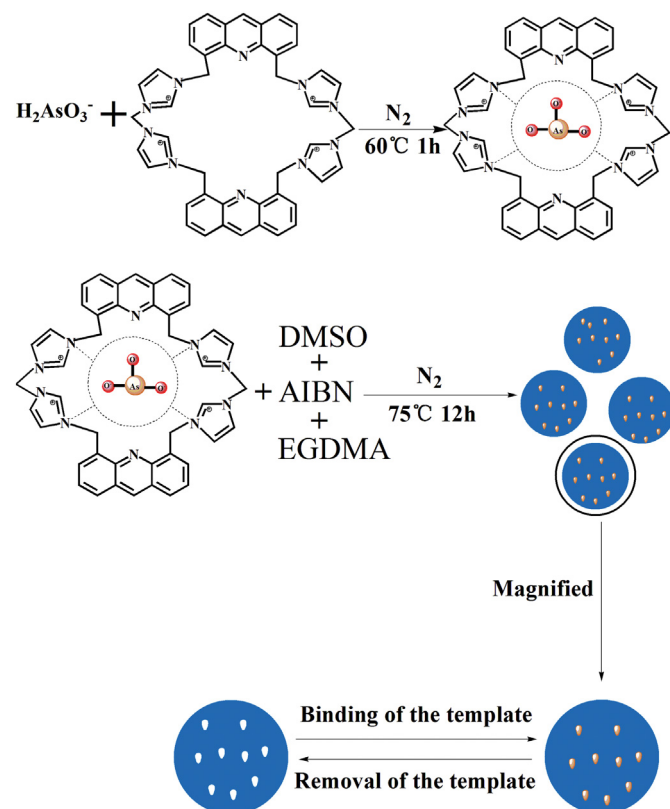


Fig. 1. Synthesis route of As-IIP.

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