



Zirconium/polyvinyl alcohol modified flat-sheet polyvinylidene fluoride membrane for decontamination of arsenic: Material design and optimization, study of mechanisms, and application prospects



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HIGHLIGHTS

- A Zirconium/PVA modified PVDF membrane is fabricated for arsenate removal.
- Modification enhances hydrophilicity and BSA rejection rate of membrane.
- The membrane has good performance for arsenate removal in batch and filtration modes.
- The maximum adsorption capacity is as high as 128 mg-As/g at the optimal pH 2.0.
- The uptake of arsenic is a ligand-exchange between arsenate and chloride.

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ABSTRACT

Arsenic contamination in industrial wastewater and groundwater has become an important environmental issue. In this study, a novel zirconium/polyvinyl alcohol (PVA) modified polyvinylidene fluoride (PVDF) membrane was developed for arsenate removal from simulated contaminated water. A PVDF flat-sheet membrane was first fabricated; it was then soaked in a zirconium-PVA solution and dried, and finally reacted with a glutaraldehyde solution, by which the zirconium ions were impregnated onto the PVDF surface through the ether and hydroxyl groups according to the cross-linkage mechanism. The fabrication procedure was optimized by the Box-Behnken experimental design approach. The adsorption kinetics study showed that most of uptake occurred in 5 h and the equilibrium was established in 24 h. The acidic condition was beneficial for the arsenate removal and the optimal removal efficiency can be obtained at pH 2.0. The experimental data of the adsorption isotherm was better described by Langmuir equation than Freundlich equation. The maximum adsorption capacity of 128 mg-As/g was achieved at pH 2.0. In the filtration study, the modified membrane with an area of 12.56 cm² could treat 15.6 L arsenate solution (equivalent to 75,150 bed volumes) with an influent concentration of 98.6 μg/L to meet the maximum contaminate level of 10 μg/L. Several instrumental studies revealed that the removal was mainly associated with ion exchange between chloride and arsenate ions.

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1. Introduction

Heavy metal contamination has become a serious environmental issue over the past few decades. Among various heavy metals, arsenic contamination in natural water is a great threat to humans as it can cause a series of health problems even when its concentration is at low levels (Clewell et al., 2011; Cui et al., 2012; Baig et al., 2015). Since 1975 the US Environmental Protection

Agency (USEPA) had set the maximum contaminant level (MCL) of arsenic as 50 μg/L for drinking water. Furthermore, the USEPA has updated the standard to a lower concentration of 10 μg/L for drinking water since 2006 (Zhang, 2010).

Main arsenic removal technologies are oxidation, coagulation, ion-exchange, adsorption and membrane filtration (Oehmen et al., 2011; Richards et al., 2011; Yang et al., 2011; Zheng et al., 2012a). Among them, adsorption and membrane filtration are the most extensively studied methods for arsenic removal owing to high efficiency and ease in operation. However, such disadvantages as generation of arsenic-contaminated solid wastes and high energy

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cost have limited their wide applications in the treatment of arsenic contaminated water (Brandhuber and Amy, 1998).

Among various sorbents, zirconium based adsorbents for arsenic removal have been reportedly studied zirconium oxide (Hang et al., 2011), zirconium impregnated collagen fiber (Liao and Shi, 2005), zirconium loaded lysine diabetetic acid resin (Balaji et al., 2005), zirconyl-functionalized activated carbon (Schmidt et al., 2008) have attracted wide attentions.

Being a hard Lewis acid metal, zirconium-based sorbents show higher affinity towards arsenic (Blackwell and Carr, 1991). The unsaturated electronic orbit of zirconium can accept electron pairs from other species, in which the electron pair donors could be coordinated to the available sites (Blackwell and Carr, 1992). In view of the specific advantages of the zirconium based adsorbents, it is important to develop more effective zirconium based materials for the arsenic removal.

Since the positively charged zirconium ions can form complexes with such functional groups as amino, carboxyl and hydroxyl groups through Lewis acid-base pair, they may directly be grafted onto such materials as polyvinyl alcohol (PVA) that have abundant hydroxyl groups on the polymer chain. Although, the PVA has a good film-forming property and is suitable in membrane fabrication (Praptowidodo, 2005; Zhang et al., 2006), the mechanical strength of the PVA membrane is relatively low. As a result, it can only be used as a coating or blending material together with traditional membrane forming polymers (Tang et al., 2009; Caprarescu et al., 2015; Li et al., 2015).

To overcome the aforementioned drawback of the PVA, a membrane can be first used as a supporting layer. Poly (vinylidene fluoride) (PVDF) membrane can be fabricated as a support layer as it has such outstanding properties as high mechanical strength, thermal stability, chemical resistance, and hydrophobicity (Liu et al., 2011; Kang and Cao, 2014). The modification of PVDF membrane was successfully conducted with PVA as a coating layer to enhance the anti-fouling property of membrane (Du et al., 2009). The cross-linkage of PVA polymer can be obtained by using the glutaraldehyde as a cross-linkage agent. It was reported that some nanoparticles can be grafted onto PVA polymer chain by the glutaraldehyde (Liang et al., 2013; Qin et al., 2015).

In this study, we developed a Zr/PVA modified PVDF membrane through surface modification of PVDF membrane by the PVA and the zirconium so that it can be used to remove the arsenic from water solutions. This novel membrane is better than the traditional water treatment materials such as adsorbents and ion exchange resins. For instance, it is able to effectively remove arsenic through filtration process without producing arsenic-containing solid wastes. It can simultaneously remove other contaminants in water such as natural organic matters, microorganisms and suspended solids.

The membrane properties, such as morphologies, hydrophilicity, water flux, mechanical strength were evaluated in details. A series batch adsorption and filtration experiments for arsenate removal were conducted to obtain the key operational experiments parameters for the removal. The mechanism was also investigated by the X-ray photoelectron spectroscopy (XPS) and quantification of changes in chloride and arsenate in water.

2. Materials and methods

2.1. Materials

All the chemicals used in this study were of analytical grade without further purification. The sodium arsenate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$) and the PVA with the M_w of 72,000 g/mol and a degree of polymerization of 1700 were obtained from Fluka (Switzerland).

The zirconium oxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) was purchased from Tianjin Chemical Co., Ltd. (China). The PVDF powder ($M_w \sim 180$ kDa), the dimethylacetamide (DMAc), the glutaraldehyde (GA) aqueous solution (Grade II, 25%), the bovine serum albumin (BSA, $M_w \sim 66$ kDa), the humic acid (sodium salts, Catalogue Number: H16752) and other chemicals used in this study were purchased from Sigma-Aldrich (Singapore).

2.2. Fabrication of PVDF membrane

The PVDF flat sheet membrane was fabricated through phase-inversion method as the following steps. The membrane polymer solution was prepared by dissolving 18 wt% PVDF into 82 wt% DMAc at 70 °C for 12 h. After degassed by an ultrasonic device, the polymer solution was casted on a non-woven fabric and then immediately immersed into the coagulation bath of deionized (DI) water. The solidified membrane was rinsed by the DI water and kept in the DI water for further experiments.

2.3. Surface modification of PVDF membrane

The schematic illustration of the surface modification of the PVDF membrane is given in Scheme 1. Firstly, an alkaline treatment was conducted to introduce hydroxyl groups on the surface of the membrane and improve the hydrophilicity (Brewis et al., 1996; Ross et al., 2000, 2001). The PVDF membrane was then treated with a mixture solution of 4 wt% KMnO_4 and 20 wt% KOH at 60 °C for 45 min, and subsequently immersed in another solution of 2 wt% H_2SO_4 and 2 wt% NaHSO_3 at room temperature till the membrane turned white.

The coating process of zirconium ions and PVA on the PVDF membrane was accomplished as follows: (1) A mixture of the PVA (0.2–0.6 wt%) and the zirconium oxychloride (10–60 mM) was prepared by dissolving into a 100-mL DI water. The hydrolysis of the zirconium oxychloride may be occur in the solution, which could form the hydroxyl groups; (2) 1.0-g alkaline treated PVDF membrane was soaked in the PVA-Zr mixture for 5 h, and the membrane was taken out and dried in air; (3) The dried membrane was then soaked in a mixture of glutaraldehyde (1–2 wt%) and the hydrochloric acid (1–19 mM); the cross-linkage reaction was conducted at 45 °C for 2 h; and (4) the membrane was finally washed by the DI water to remove the unreacted zirconium ions, PVA and GA.

2.4. Box-Benhken experimental design and optimization

The optimization of cross-linkage reaction was conducted by a Box-Benhken experimental design with four factors with three levels, which were combined with the response surface modeling. The dosages of PVA, zirconium oxychloride, GA (crosslinking agent) and hydrochloric acid (catalyst) were selected as the independent factors. The adsorption capacity of arsenate (q) at equilibrium was chosen as the response in the optimization. Testing of the four factors was conducted at three levels, coded as -1 , 0 , $+1$ for the low, center and high values, respectively. The input factors were PVA dosage (X_1), zirconium dosage (X_2), GA dosage (X_3) and HCl dosage (X_4). The four-factor Box-Behnken design required 29 runs, which included 5 center points experiments. This experiment was replicated and a total of 58 experiments were carried out. The coded and true values of the four factors were shown in Table S1.

Design Expert 8.0.6 (Stat-Ease Inc., Minneapolis, USA) was used to design the experiment. The design matrix of the Design Expert would provide a suitable model for predicting the optimal response. The possible interactions between the four factors were shown below:

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