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Regular Article

Construction of hydrophobic alginate-based foams induced by zirconium ions for oil and organic solvent cleanup

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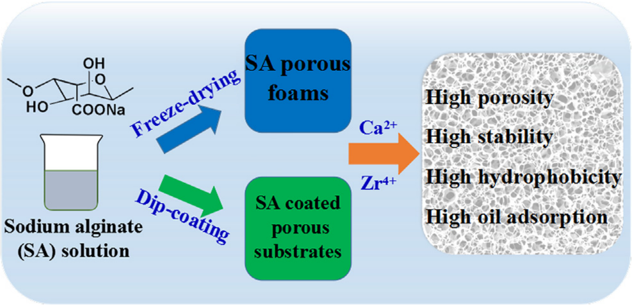
GRAPHICAL ABSTRACT



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ABSTRACT

Hydrophobic modification of sodium alginate (SA) foams via a simple freeze-drying and post cross-linking induced by zirconium (Zr) ions was developed. All results demonstrated that Zr ions not only constructed surface microstructure but also lowered surface energy of foams, leading to the hydrophobic character. Hydrophobic and oleophilic foams showed excellent adsorption capacities for different oils and organic solvents (11.2–25.9 g/g). Furthermore, SA solution can be also coated on porous substrates, such as melamine sponges (MS) and Nylon strainers (NS), to give hydrophobic modification by Zr ion crosslinking. These excellent performances made them a promising for oil adsorption and cleanup.

1. Introduction

Water contaminants caused by frequent oil spill or organic contaminants from petrochemical, textile, food, steel and metal finishing, have severely jeopardized animals, plants and human beings [1,2]. To date, numerous strategies such as physical adsorption, in situ combustion, biodegradation, filtration membranes, have been applied to remove oil spills [3,4]. Among them, adsorption is always viewed as a promising technique because of its high efficiency, low cost and easy operation [5,6]. In the past few years, actived carbon, zeolite, clay, and carbon nanotubes have been used as effective adsorbents for oils and organic solvents cleanup [7–9]. However, these traditional composites are powdery and difficult to be separated and recovered in industrial applications [10]. Moreover, they may generate secondary pollutants due to itself leakage, particularly in flowing streams [10,11]. Recently, various wettable materials especially three-dimensional (3D) adsorbent materials have become one of the most attractive materials for oil-spill cleanup [12].

To effectively separate oil from water, oil absorbents possess hydrophobic and oleophilic property [13]. In general, low surface

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energy and rough micro-/nanostructure were key prerequisites to construct hydrophobic surfaces [14,15]. According to above principle, much significant efforts have been devoted to developing oil adsorbents using common strategies including dip-coating method [16], spray-coating method [17], solvothermal method [18] or in situ growth method [19]. In our previous work, we demonstrated hydrophobic modification of melamine sponge (MS) using poly(furfuryl alcohol), forming a hydrophobic layer via dip-coating method [20]. These as-obtained MS exhibited excellent adsorption capacities for various oils and organic solvents (75–160 g/g). In another typical example, Zhu et al. fabricated superhydrophobic foams with graphene via one-pot thermal reduction method [21]. During the thermal reduction process, reduced graphene oxide (rGO) was self-assembled on 3D skeletons, and thus surface energy and roughness were improved dramatically. Although these extraordinary materials have shown a promise for oil treatment, there are still some challenges and drawbacks to be overcame, such as using expensive modifying agents, slow biodegradability as well as environmental problems caused during the preparation process. In this respect, novel biomass-based oil adsorbents materials have become a rising star because of their extensive sources, renewability and biodegradability [18,22]. As a significant example, Feng et al. prepared centimeter-sized porous carbon spheres oils adsorbent via carbonization of the fruit of Liquidambar formosana [23]. Remarkably, it has been recognized as a good choice to develop hydrophobic biomass-derived adsorbents for oil/water separation applications [24,25].

Sodium alginate (SA) consists of β-(1-4) linked D-mannuronic acid (M unit) and α-(1-4) linked L-guluronic acid (G unit), arranged in blocks aboundant in G units (…GGGGG…), blocks abundant in M units (…MMMMM…), and blocks of alternating G and M units (…GMGMGM…) [26,27]. Furthermore, it is a low-cost, non-toxic, and renewable polysaccharide containing many functional groups (e.g. —COONa and —OH) [28,29]. It can also form hydrogels by ionotropic gelation with divalent ion (Ca^{2+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, Ba^{2+}) [18,30,31], trivalent ions (Ce^{3+}, Al^{3+}, Fe^{3+}) [32–34], quadrivalent (Zr^{4+}) [35,36] and even free metal ions (hydrochloric acid, oxalic acid) [37]. However, the hydrophobicity of SA crosslinked by Zr^{4+} was ignored owing to micron size and oxygen-containing groups. Recently, we have synthesized 3D alginate-based foams via Ca^{2+} crosslinking for heavy metal ions (Cu^{2+}, Cd^{2+}) removal [38]. Unfortunately, Ca^{2+}-induced SA foams were intrinsically amphiphilic absorbents, usually absorbing both water and organic chemicals simultaneously. So it was restricted for selective oil adsorption from water with high efficiency.

In this work, we offered a new strategy to design hydrophobic SA foams for oils adsorption by ionic crosslinking method. Amphoteric SA-Ca foams were crosslinked with Zr ions to improve hydrophobic property. To our knowledge, ion-induced hydrophobicity in SA-Ca foam has not been reported previously. The hydrophobicity of SA-based foams is characterized by Scanning electron microscopy, X-ray photoelectron spectroscopy and Fourier transform infrared spectra. Furthermore, the versatility of SA was demonstrated as well. Hydrophobic performance and oil adsorption capacity of porous substrates, such as MS and Nylon strainers (NS), coated with SA hydrophobic coatings were also investigated.

2. Experimental section

2.1. Chemicals

Sodium alginate (analytical reagents, SA) was purchased from Sinopharm Chemical, China. Zirconyl chloride octahydrate ($ZrOCl_2·8H_2O$) was obtained from Shanghai Titan, China. Anhydrous calcium chloride (analytical reagents, $CaCl_2$) was purchased from Xilong Scientific Co., Ltd., China. Nylon strainers with 180 mesh were obtained from local supermarket. Commercial melamine sponges (LD-1539F, $8 \times 5 \times 2.5\ cm^3$) were bought from Ledian householship store, Zhejiang, China.

2.2. Synthesis of sodium alginate-based foams

3D hydrophobic SA foams were fabricated as follows. 1 g of SA was dissolved in 25 ml of deionized water to form clear and viscous slurry. Then SA slurry was injected into a cubic mould with a size of $1 \times 1 \times 1\ cm^3$ by a syringe, followed by lyophilization overnight to prepare SA foams. Subsequently, these obtained SA foams (1 g) were impregnated in 200 ml of $CaCl_2$ solution (5 wt%) and kept for 4 h to develop calcium alginate (SA-Ca) foams. The perpared foams were washed several times with deionized water to remove residual $CaCl_2$ solution. After that, SA-Ca foams were soaked in 200 ml of $ZrOCl_2·8H_2O$ solution (3 wt%) and maintained for 4 h for the crosslink reaction at ambient temperature. The resulting foams were obtained after washing until the pH of solution from acidity to neutrality and then freeze-dried again, and it was denoted as SA-Ca-Zr foams. SA-Zr foams were synthesised by the same method as above without using $CaCl_2$ solution.

2.3. Characterizations

Surface functional groups of composite materials were detected by a Fourier transform infrared spectra (FTIR) spectrophotometer (Thermo Electron Nicolet-360, USA). The surface morphologies and micro-/nanostructures were recorded by scanning electron microscopy (SEM) utilizing a FEI-Quanta200 (America). Elemental analysis was explored using Energy-dispersive X-ray spectroscopy (EDX) attached to the microscope. Contact angle analysis (JC2000D1, Shanghai Zhongchen Digital Technic Apparatus Co., Ltd., China) was used to measure the surface wettability of samples. The surface chemical bonds was studied with X-ray photoelectron spectroscopy (XPS, AXIS UltraDLD, Japan).

2.4. Measurement of porosity of SA-Ca-Zr foams

SA-Ca-Zr foams were completely immersed in absolute ethanol for about 1 min and then removed for measurement [39]. The porosity of SA-Ca-Zr foam was calculated as follows Eq. (1):

$$\text{Porosity}\,(\%) = (m - m_0)/(\rho \times v) \times 100 \tag{1}$$

where m_0 (g) and m (g) stand for the mass of foam before and after ethanol saturation, respectively. ρ is the density of absolute ethanol (0.789 g/cm^3), and v represents the bulk volume of the SA-Ca-Zr foam.

2.5. Oil and organic solvent adsorption

All kinds of organic solvents and oils such as dimethylformamide, *n*-hexane, acetone, chloroform, toluene, tetrachloromethane, paraffin liquid, cyclohexane, ethyl alcohol and soybean oil were employed in this work to evaluate adsorption capacities of modified foams by weighing method. In brief, rectangular foams were preweighed and then immersed in different organic solvents or oils without water for ca. 1 min to reach adsorption equilibrium. After that, these saturated foams were held in air for ca. 1 min to remove excessive oils or solvents before weighing [40]. The adsorption capacity of SA-Ca-Zr foams was calculated according to Eq. (2):

$$Qe = (m - m_0)/m_0 \tag{2}$$