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Separation of heavy metals from water by functionalized glycidyl methacrylate poly (high internal phase emulsions)☆

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ABSTRACT

Removal of silver, lead and cadmium ions from both model solutions and real contaminated water was achieved, in a flow through manner, by using highly porous functionalized poly(glycidyl methacrylate) materials, prepared by the polymerisation of high internal phase emulsions (polyHIPE), with significant sorption differences between metals allowing for selective removal. PolyHIPEs, initially prepared from glycidyl methacrylate as a functional monomer, were functionalized with pentaerythritol tetrakis(3-mercaptopropionate), 1,9-nonanedithiol and 2-aminobenzenethiol via the epoxy ring opening on the polymer supports and applied in a flow-through manner via encasements into dedicated disk holders. Capacity of 21.7 mg Ag per gram of polymer was found for 1,9-nonanedithiol functionalized polymers, while the capacity was decreasing with the decreasing ionic radius of the metal; the dynamics of sorption also depended on metal ion size and furthermore on the thiol used for the polymer functionalization.

1. Introduction

Due to the toxicity of most heavy metals and their presence in natural environment as a result of pollution, much research has been devoted to the development of efficient and inexpensive methods for the removal of heavy metals from the environment, especially water. Most commonly used methods are chemical [1–5] and biological precipitation [6,7], adsorption [8,9], physical [10,11] and electrochemical separation [12–14], flotation [15] and ion-exchange [16,17]. In precipitation processes, chemicals or biological substances react with heavy metal ions to form insoluble precipitates, which are then separated by sedimentation or filtration. By adsorption, metal ions are adsorbed on a surface of an activated material and can be also regenerated by a desorption process. Method is inexpensive but can lead to an undesired desorption. Physical separation includes a barrier, which disables metal ions to flow through and electrochemical separations involving a cathode, which can recover metals in their elemental state. Both methods are expensive and are therefore rarely used. Flotation process includes a surface-active agent, which causes a surface non-active "metal" to become active and can be removed by bubbling gas.

Due to specific morphological architecture and open porous morphology, polymers prepared by emulsion templating method (polyHIPEs) are a good candidate for heavy metal ion removal [18]. PolyHIPEs are highly porous polymeric materials prepared by the polymerisation of high internal phase emulsions [19,20], which are prepared by an addition of a large portion of internal phase to the continuous phase and stabilised typically by the addition of surfactants. After the polymerisation, materials with a typical interconnected porous morphology, consisting of large primary pores (cavities) and smaller interconnecting pores, are obtained (Fig. 1).

Interconnected porous architecture is especially welcome in the case of applying polymeric columns for flow reaction systems. Most commonly used and best-studied systems for the preparation of HIPEs is based on styrene and its derivatives but recently a wide range of monomers has been used within this approach [21]. Glycidyl methacrylate (GMA) has also been demonstrated as a possible monomer for the preparation of polyHIPEs [22–25]. It raised significant interest due to hydrophilicity and possible functionalization via nucleophile attack resulting in the opening of the epoxy ring. For heavy metals binding a polymer immobilized thiol functionality is preferred due to the strong metal–sulphur interaction. Recently, an example of a functionalized polyHIPE material for the removal of heavy metal from aqueous media has been demonstrated by Mert

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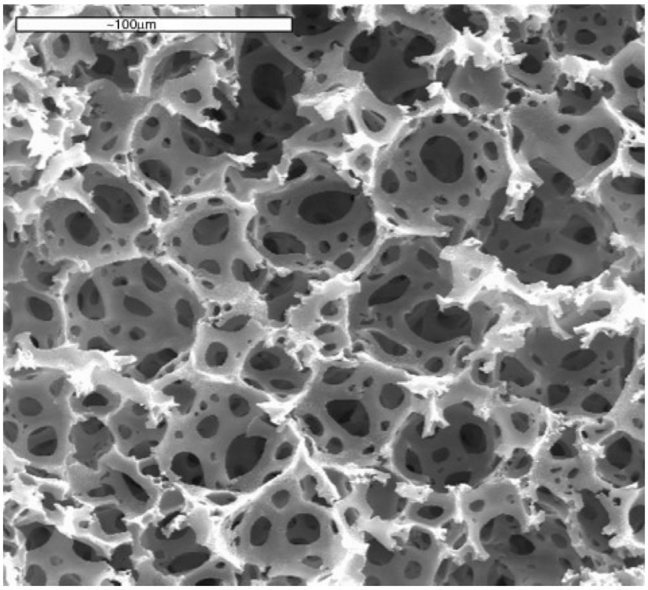

Fig. 1. SEM image of a typical polyHIPE structure. Bar is 100 µm.

et al. [18], while a functionalised polyHIPE has also been used for the removal of atrazine pesticides from water [26].

In this study, the preparation of new functional polyHIPE materials, directly modified with pentaerythritol tetrakis(3-mercaptopropionate), 1,9-nonanedithiol and 2-aminobenzenethiol are reported and the heavy metal uptake from aqueous solution and real sample of contaminated water are investigated.

2. Materials and methods

2.1. Materials

Glycidyl methacrylate (GMA; Sigma–Aldrich), methyl methacrylate (MMA; Sigma–Aldrich) and ethylene glycol dimethacrylate (EGDMA; Sigma–Aldrich) were passed through a layer of basic alumina (Al_2O_3; Fluka) to remove the inhibitors. Surfactant poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Synperonic PEL-121, Sigma–Aldrich), initiator Irgacure 819 (I819; Ciba), calcium chloride hexahydrate ($CaCl_2 \times 6H_2O$) (Sigma–Aldrich), 2-aminobenzenethiol (AT; Sigma–Aldrich), 1,9-nonanedithiol (DT; Sigma–Aldrich), pentaerythritol tetrakis(3-mercaptopropionate) (TT; Sigma–Aldrich), isopropyl alcohol (IPA; Sigma–Aldrich), dichloromethane (DCM; Sigma–Aldrich), 2,2,2-trifluoroethanol (TFE; Sigma–Aldrich), sulphuric acid (H_2SO_4; Sigma–Aldrich), Ag(I) standard Certipur (merck) and ethanol (EtOH; Merck) were used as received.

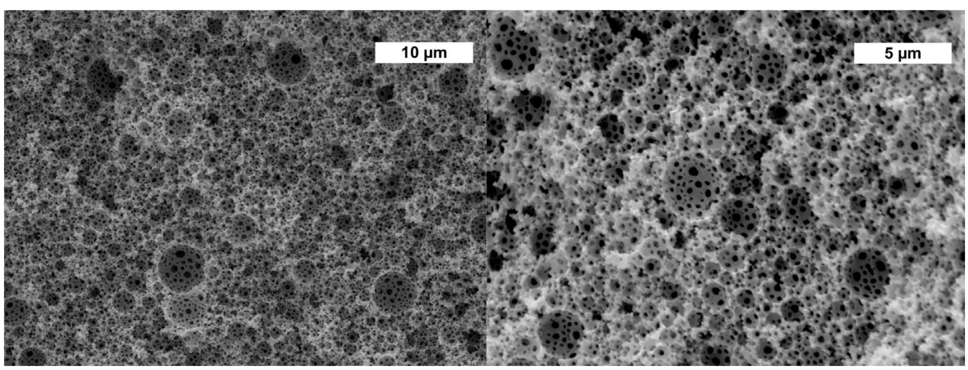

Fig. 2. SEM images of sample S0 at 2500×(left) and 5000×(right) magnification.

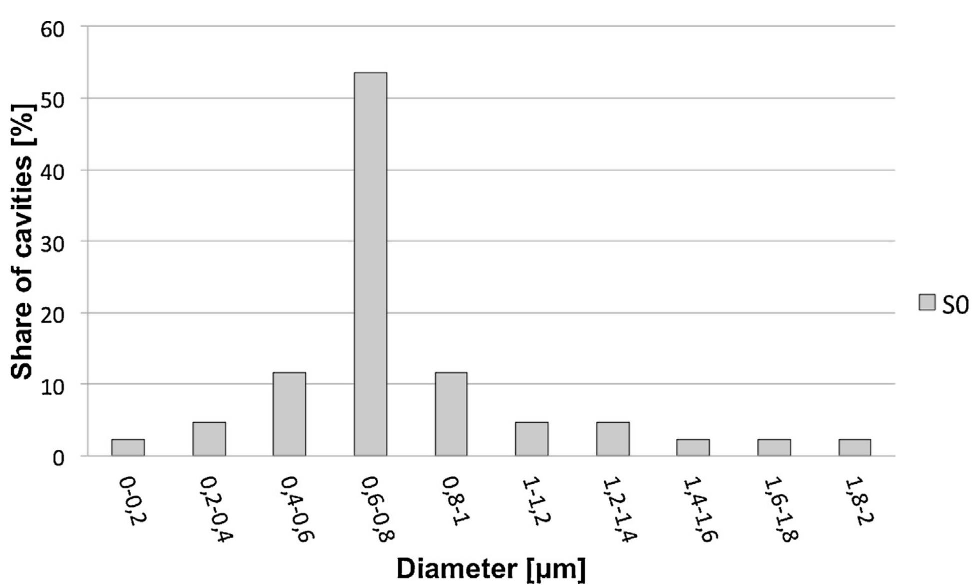

Fig. 3. Cavity size distribution of the sample S0.