MACROPOROUS HIGHLY PERMEABLE COMPOSITES WITH NANOPARTICLES

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Abstract

Macroporous permeable composites with embedded nanoparticles were prepared by cryogelation. Nanoscale particles have large surface area and high surface reactivity and provide cost effective solutions to many challenging environmental remediation problem. Embedding the nanoparticles into polymer or other substrates significantly reduces the risk of free nanoparticles release into the environment. The use of particles at micro size scale has also been investigated. The particles distribution in polymer network, mechanical properties and reactivity of composites were studied. The composite material has a unique structure of large interconnected pores which provide high permeability. Iron oxide nanoparticles and nanoporous carbon microparticles were physically embedded within the macroporous polymer which prevented their release into the environment. The composite devices showed promising results for the removal of the trace concentrations of As(III) from solution and removing trace polar organic contaminants. The interconnected large pores and low flow resistance of macroporous composites make them promising material to be used as a support for micro- and nanoparticles in developing adsorption/filtration devices.

1 Introduction

Macroporous polymers have large surface area and big pores (upto 100 μm) that have been usefully utilized in a number of different applications mainly for developing adsorbents, chromatographic materials and materials for the separation. The porous polymers are often used as a scaffold for developing of functional materials with functional groups in polymer matrix or support for adsorbent which are embedded in the polymer matrix. Embedding the particular materials in the polymer scaffold gives the advantage to produce the devices of different geometry, shape, porosity and also immobilize the particular adsorbent preventing its leakage to the environment. The composite materials is often more robust and more stabile. In this work we discuss the preparation of the permeable composites with iron oxide nanoparticles and activated carbon microparticles.

Nanoscalled particles due to their large surface area and reactivity could provide cost effective solution to many environmental problems, including polluted waters. However because of the small size it is quite challenging to produce the effective filtration/adsorption device. The columns filled with nanoparticles have low or no permeability. Moreover there is increasing number of the reports on the toxicity of manufactured nanoparticles for mammals, plants and microbes and the detrimental impact of release of the free nanoparticles to the environment. This limits the use of nanoparticles in many applications. Embedding the nanoparticles into porous meso/macro matrix is a safe approach for the designing the nano-based adsorption materials.

In our previous work we have designed a macroporous polymer filter where the particles were embedded inside the polymer matrix [1]. This was a 3D scaffold produced by using cryogelation technology [2, 3, 4]. The cryogelation technology allows to prepare porous materials with large pores upto 100 μm and highly permeable [2, 3, 4]. The particles were embedded inside the polymer scaffold and their leaking to the environment was minimum [1]. The materials has been shown the promising results for removing the arsenic(III) and traces of organic compounds from the water [1, 5]. However, there was a challenge to produce the composites with uniform distribution of the particles and overcome their deposition during the polymerization, that resulted in formation of composites with non-uniform distribution of particles along the sample. The non-uniform distribution of adsorbent in the material limits the application of such materials. In this work we explore other approaches for the development of the macroporous composite adsorption/filtration devices.

2 Results and Discussion

2.1 Production of macroporous composites with nano-particles

2.1.1. Effect of Laponite RD content onto the iron oxide deposition during hydrogel formation

Laponite, a synthetic layered silicate is quite often used as an additive for improving the physico-mechanical properties of a wide range of industrial and consumer products. The small concentrations of Laponite considerably change the rheological properties of solutions. Laponite RD was added to the reaction solution to prevent the deposition of Fe_3O_4 nanoparticles during the polymerization. The increase of Laponite RD content resulted in the increase the reaction solution viscosity that reduces the deposition of Fe_3O_4 nanoparticles during the gel formation (Figure 1). Adding 1-2 % of Laponite RD considerably reduced the deposition of Fe_3O_4 nanoparticles in the both prepared at room temperature and at -12 °C gels (Figure 1).

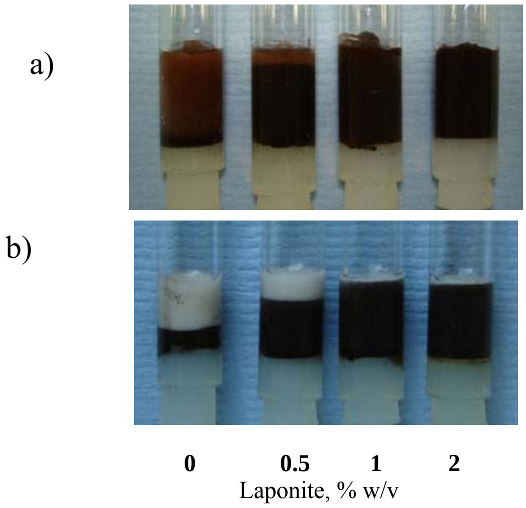


Figure 1. Effect of Laponite RD content onto the iron oxide deposition during HEMA hydrogel formation: a) gels prepared at room temperature (conventional gels) and b) gels prepared at – 12 °C.

The increase of Laponite RD content from 0 to 1% resulted in increase the compression modulus for both conventional (prepared at room temperature) and macroporous (synthesized at -12 ^{o}C) gels (Figure 2). The compression modulus of gels with 2% Laponite RD was found to be lower than for gels with 0.5 and 1% of Laponite RD. Moreover the gels become more fragile with increase of Laponite RD content. In general the gels prepared by cryogelation were more elastic and mechanically strong, compared to conventional gels made by polymerization at room temperature. The gels made by freezing have shape memory and recover their shape after compression (Figure 2). They have sponge like morphology and interconnected pores, which makes them promising material for developing adsorption/filtration devices.

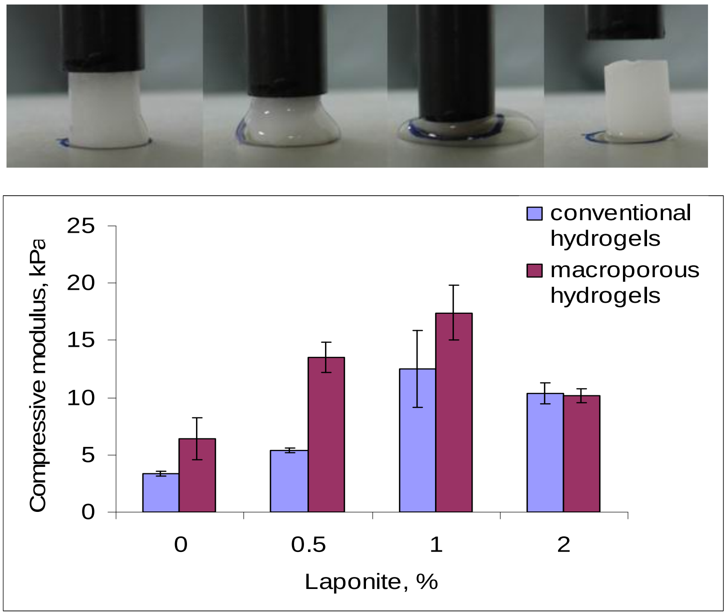
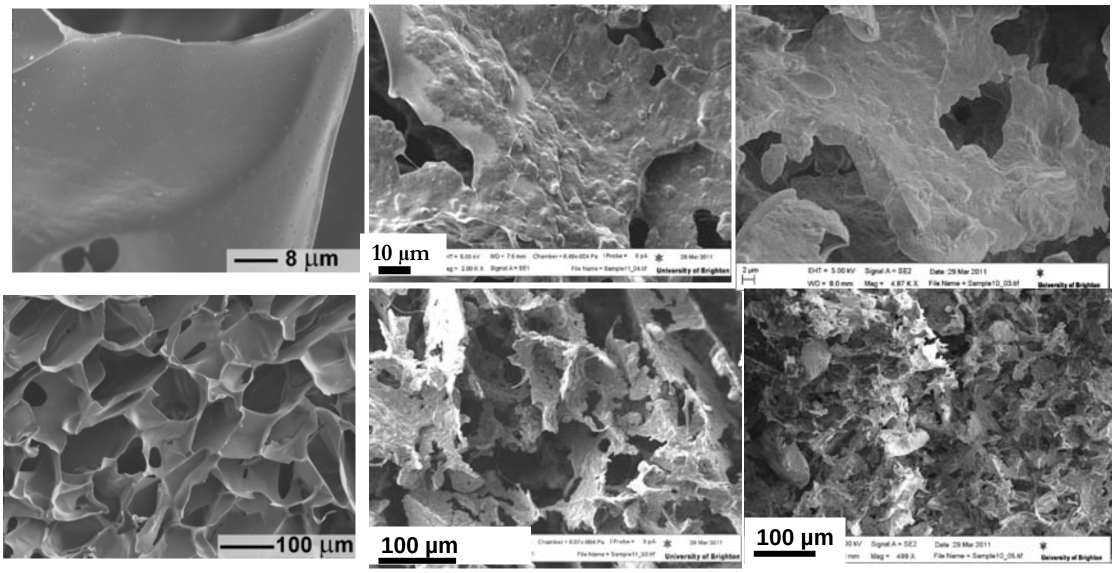


Figure 2. Compressive modulus of HEMA hydrogels with different Laponite RD content.

The fragility of the composite gels with higher content of Laponite RD could be explained by few factors: effect of Laponite RD particles on mechanical properties and the morphology (porosity) of the material. SEM image analysis shows that the Laponite RD and Fe_3O_4 nanoparticles are embedded inside the polymer wall (Figure 3). The gels with higher Laponite content have smaller pores and less dense polymer walls. The different porous structure may result from adding Laponite RD and its effect on the freezing of polymer solution and ice crystal formation. The re-distribution of the monomers/polymers phase during the freezing-out the solvent will be slower in more viscous solution with higher Laponite RD content. The presence of Laponite RD particles may initiate an ice nucleation leading to formation of higher number of small ice crystals compared to the freezing of solution without added Laponite RD. As result, smaller pores are formed and material has less dense polymer wall (Figure 3).

2.1.2. Preparation of composites from the suspension of the fresh made akaganeite nanoparticles.

Composites with akaganeite particles were prepared as adsorbent materials for the water purification. Akaganeite nanoparticle freshly made suspension was used for making the macroporous gel. Acrylamide (AAm) and HEMA gel were prepared. No particle distribution in the sample was observed. The freshly prepared akaganeite forms stabile suspension, but after drying the nanoparticles were fount to not disperse homogeneously in solution. Thus we have directly used the purified nanoparticle suspension for the gel formation. As could be seen on TEM image the nanoparticles have been evenly distributed inside the polymer wall (Figure 4). The analytical analysis of the column samples taken from the top, the middle and the bottom has shown the iron content 2.75, 2.66 and 2.62 % without significant difference among them. The gels made from acrylamide were harder and have higher compressive modules 173 kPa comparing to HEMA gels, 29 kPa (Table 1)



Laponite RD: **0 %** **0.5%** **1%**

Figure 3. Scanning electron microscopy images of HEMA gel and HEMA composite gel with Laponite RD and iron oxide.

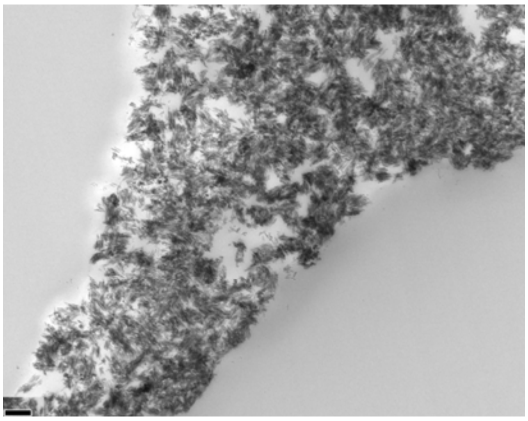


Figure 4. TEM image of acrylamide gels with akaganeite nanaporticles. The bar is 0.2 µm.

Sample	Compressive modulus, kPa
Ak-AAm	173±62
Ak-HEMA	29±6

Table 1. Compressive modulus of macroporous gel with akaganeite (Ak).

2.2. Permeability

The permeability of the macroporous gels was analysed by pumping an aqueous solution through the macroporous gel. The flow resistance and compression of the gel monolith at different flow rate is presented in Figure 5.

The HEMA gel without Laponite RD started to compress at flow rate > 1 ml/min and showed flow resistance at flow rate > 4 ml/min. Compression of the gel resulted in blocking/closing the pores that decreased the column permeability and caused backpressure (Figure 5).

The gel with Laponite RD showed better permeability. The aqueous solution could be pumped with flow rate up to 8ml/min without any flow resistance (Figure 5). The composite gel started to compress at flow rate >3.8 ml/min, however it did not effect to the permeability. The composite gels with Laponite RD had more rigid polymer walls, thus even under the gel compression the permeability of the whole column did not changed significantly. The AAm macroporous gel could withstand the higher pressure without compression. Thus the aqueous solution was pumped through the Akaganeite-AAm column at 15 ml/min (Figure 5).

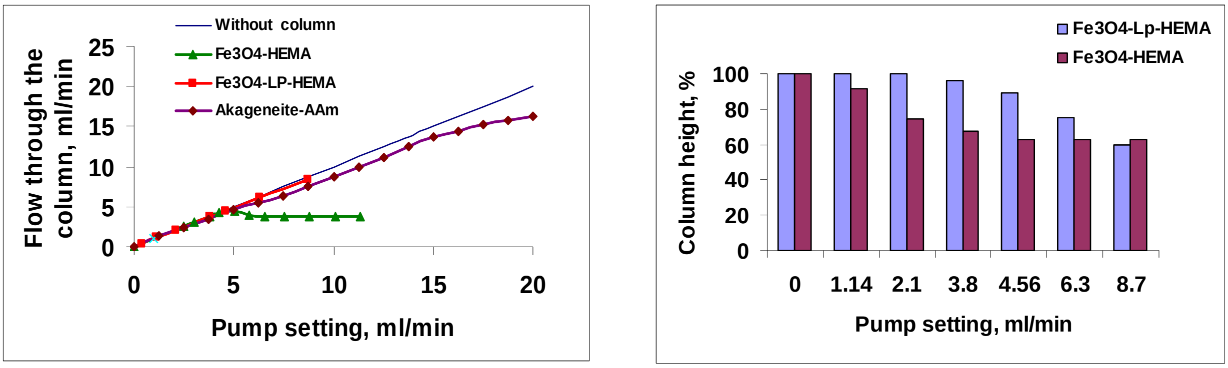


Figure 5. Flow resistance (a) and compressibility (b) of HEMA composites with Laponite RD and iron oxide nanoparticles.

2.3. As (III) adsorption

The composites have shown promising results for the removal of As(III) from the water [1]. Embedding of the nanoparticles inside the polymer did not significantly reduce the adsorption properties of the iron oxide nanoparticles (Table 3).

Samples	**As(III) mg/g of iron oxide particles**	**As(III) mg/ ml of gel**
Fe_2O_3 loose particles	8.96 ±1.6	NA
Fe_3O_4 loose particles	9.63 ±2.4	NA
HEMA-macroporous gel	NA	0.008
HEMA macroporous gel with Laponite (0.5%)	0	0
HEMA Fe3O4, 0.15 g/ml	4.06±0.3	0.61±0.05
HEMA Fe3O4m (0.15 g/ml) and Laponite (0.5%)	4.46±0.2	0.67±0.03
HEMA Fe2O3 (0.15 g/ml) and Laponite (1.0%)	5.2±0.53	0.78±0.08

Table 3. Equilibrium adsorption capacity for As(III).

2.4. Monolithic porous polymer structure (MPPS®) embedding activated carbon particles as adsorption filtration devices

Macroporous PVA gels with activated carbon particles (MPPS®) were studied as well. The gels were provided by Protista Biotechnology AB and they have been prepared using the cryogelation technology similar to the one used for nanoparticles composites preparation. The filter contains carbon particles, produced at MAST Carbon International Ltd. The carbon particles have high surface, in the range of 2000 m^2/g, and porosity tuned to trap small-size polar contaminants. The high porosity of the monolith (Figure 6) allowed filtering water with flow velocities in the same range as used in industrial scale while providing higher purification of polar contaminants than conventional adsorption treatments carried out in water treatment plants using granulated activated carbon. The embedding of the beads in a PVA matrix reduced the active surface, decreasing the atrazine removal by 39% but still offered an improvement compared to other technologies [5]. The homogeneous distribution of microcarbon beads provides high purification efficiency for removal of polar organic contaminants from water [5].

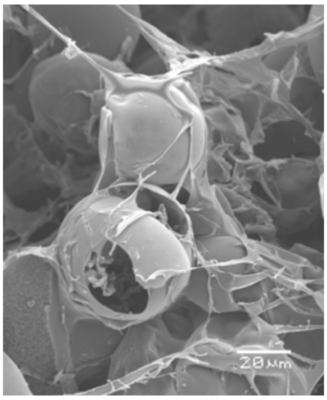


Figure 6. SEM image of the carbon beads embedded in a PVA cryogel (Protista AB).

3 Materials and testing methods

3.1. Materials

2-hydroxyethyl methacrylate (HEMA, 98%) was sourced from Acros Organics (Geel, Belgium). Poly(ethylene glycol)diacrylate (PEGDA, M_n ~ 258), acrylamide (AAm) and methylene-bis-acrylamide (MBAA) were obtained from Aldrich (Steinheim, Germany). Ammonium persulfate (APS, 98%) and N,N,N,̀Ǹ-tetramethylethylenediamine (TEMED, 99%) were from Thermo Scientific (Rockford, USA). Iron nanoparticles α-Fe_2O_3 and Fe_3O_4 were obtained from Arry International Group Limited (Köln, Germany). Average particle size was 30 nm and 20 nm for α-Fe_2O_3 and Fe_3O_4, respectively. Akagenite nanoparticles were supplied by Dr. M. Vaclavikova group. Carbon-PVA composites were supplied by Protista Biotechnoloy AB (Bjove, Sweden, www.protista.se) As (III) oxide was obtained from Argos Chemicals (New Jersey, USA). Laponite was kindly supplyied by Rockwood.

3.2 Macroporous monolith preparation

Monolithic macroporous composite gels were prepared by the polymerization of different monomers: HEMA was co-polymerized with PEGDA and AAm was co-polymerized with MBAA. Iron oxide gel/ particles were mixed with a monomer solution. The reaction mixture was placed in an ultrasonic bath for 30 min and then cooled in an ice bath for 10 min. The reaction mixture was shaken again to obtain a homogeneous distribution of the iron oxide gel

/particles, and then TEMED/APS (1.2 w/w % of monomer) were added. 1 ml of the reaction solution was quickly added into separate glass tubes (80 x 11 mm i.d.) that were closed at the bottom with a silicon cap. The solution in the tubes was frozen in a Julabo cooling chamber at -12, incubated at that temperature for 18 hours and then thawed at room temperature. The caps were removed and gels were washed by passing 50 ml of deionised water through each sample.

3.3. Macroporous gel with Laponite RD

Laponite RD was dispersed in the water under constant stirring for 1 h. HEMA (5.8 v/v %) and PEGDA (1.7 v/v %) were added and solution degassed at low pressure for 10 min. TEMED/APS (1.2 w/w % of monomer) were added. One ml of the reaction solution was quickly added into separate glass tubes (80 x 11 mm i.d.) that were closed at the bottom with a silicon cap. The samples was let to gel at room temperature for 20 h making conventional gels. In order to prepare macroporous gels the samples was frozen in a Julabo cooling chamber at -12 ^{o}C as described above.

3.4. Permeability measurements

The flow rate of liquid passing through the column was measured at a constant hydrostatic pressure equal to a 100 cm head of water-column, which corresponds to a pressure of ca. 0.01 MPa on the cryogel composite [4].

The gel monoliths were packed in the glass column with upper and bottom adapters, which was connected to calibrated peristaltic pump. The total volume of the gel column was 4 ml. The water was pumped through the column using peristaltic pump. The pumping speed increased from 0.4 ml/min up to 10 ml/min with step 1-2 ml/min. Fraction were collected for 15 min for each pumping speed and fraction volume was measured. The length of the gel column was measured during the whole experiment.

3.5. Mechanical properties

Mechanical properties of the gels were tested using a texture analyzer with a cell load of 0.01 N. The hydrogel samples (cylinders of 10 mm height with diameter 9 mm) were placed between two compression plates and compressed with a steadily increasing compression pressure of 5 N/min to the maximum loading 18 N. All samples were tested at room temperature. Compression modulus were obtained from the stress-strain curve.

3.6. Transmission electron microscopy (TEM) and Scanning electron microscopy (SEM)

The gel samples were dehydrated by washing with ethanol water mixtures with increasing ethanol concentration of 10, 20, 30, 50 and 75% ethanol for 20 min each and dried in absolute ethanol. Ethanol was replaced with propylene oxide, which then was replaced with TAAB low viscosity resin (TAAB Laboratories Equipment Ltd, UK). After complete replacement, the resin was polymerized at 60 ^{o}C. Thin (100 nm) sections were cut on a Leica Ultracut ultramicrotome, collected on nickel support grids and examined unstained with a Hitachi-7100 TEM at 100 kV. Images were acquired digitally with an axially-mounted (2K x 2K pixel) Gatan Ultrascan 1000 CCD camera (Gatan UK, Oxford, UK).

Samples for scanning electron microscopy were prepared by freeze-drying the hybrid gels overnight. After drying, specimens were mounted on aluminium stubs fitted with adhesive carbon pads, sputter coated with platinum and examined using a Zeiss NTS EVO or Zeiss NTS Sigma FEG scanning electron microscopes.

3.8 As(III) solution preparation

A stock solution of As(III) was prepared as follows. Powdered arsenious oxide (2.5 g, As_4O_6) was dissolved in sodium hydroxide solution (2 g in 20 ml of deionised water). The volume was adjusted with deionised water to 200 ml. The pH of the solution was adjusted to 6.5 and 2 g of sodium bicarbonate was added. Finally the volume of solution was made up to 500 ml. The stock solution was then used throughout all experiments for preparation of arsenic (III) solution of varying dilutions.

3.9. Assessing the adsorption capacity of iron nanoparticles and composite gel

The gel (0.5 ml) was cut into small cubic pieces of 2 mm in size. 200 ml of 2 mg/L As(III) solution were added, the sample was shaken for 24 h at room temperature, then the As concentration was measured using a Perkin Elmer Optima^{TM} 2100 DV ICP-OES system.

Nanoparticles (20, 60 and 80 mg) were weighed in centrifuge tubes, then 20 or 40 ml of As(III) solution (4 mg/L) was added and samples were shaken for 24 h at room temperature. Nanoparticles were separated from the solution by centrifugation, 5 ml aliquots were removed and the As(III) concentration was measured. As(III) concentration before and after adsorption were measured using a Perkin Elmer Optima^{TM} 2100 DV ICP-OES system.

Conclusion

Composite materials prepared by polymerization of 2-hydroxyethyl methacrylate, acrylamide and PVA in semi-frozen conditions has a unique structure of large interconnected pores which provide high permeability. The iron oxide nanoparticles and carbon microparticles were physically embedded within the macroporous polymer preventing their release into the environment. Adding of nanoclays (Laponite RD) improve the mechanical properties of hydrogel and distribution of iron oxide in the matrix. Using a freshly prepared suspension of alkaganeite also resulted in composites with even distribution of particles. The composite made of acrylamide had better mechanical properties and permeability. The columns of acrylamide composites could be operated at a flow rate up to 15 ml per min without any visible compression of the gel matrix. The macroporous composites showed promising results for the removal of trace concentrations of As(III) from solution. Homogeneously distributing carbon beads in PVA gels provided high purification efficiency for removal of polar organic contaminants from water. The interconnected large pores, mechanical stability and low flow resistance of composite macroporous hydrogels make them promising materials to be used as a support for nano- and microparticles in developing absorption/filtration devices for the clean-up ground water, surface waters and drinking water.

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