

105c Hybrid Polymeric/Ceramic Membranes for Water Purification

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The necessity to fulfil the societal requirements for high quality drinking water is the driving force for the development of novel and efficient methods for the purification of water. Activated carbon, the traditional way of purifying water has been, and will continue to be, useful for treatment of water for undesirable tastes and odors. However, despite its relatively broad range of effectiveness in adsorbing organic substances from aqueous solutions, it can no longer be viewed as a water treatment panacea. Thus, there is an emerging need for the development of improved, alternative purification systems (e.g., hybrid membranes, hydrophobic microgels, etc.). Microgels are crosslinked polymeric particles, usually swollen with solvent molecules. They have a wide range of applications in controlled delivery, oil recovery, removal of various molecules and ions from aqueous solutions, etc. The physicochemical behavior of these materials arises from changes in their conformation in response to external stimuli such as temperature, pH or solvents. Microgels behave like nanosponges, adsorbing materials into the particles under one set of conditions, then changing conformation and releasing them again when the environment changes. In the present study, poly(styrene/ β -cyclodextrin) P(St/ β -CD) and highly crosslinked poly(styrene/meta-diisopropylbenzene) P(St/mDIB) porous nanoparticles were prepared by emulsifier-free emulsion polymerization and by a single step swelling and polymerization method to be employed as hosts for the recovery of organic contaminants from water. The polymerization experiments were carried out in laboratory scale, water-jacketed, glass reactors of 1 and 0.5 L equipped with a six-blade impeller, an overhead condenser and a nitrogen purge line. The reaction mixture was thermostated to within ± 0.05 °C with the aid of a constant temperature bath. For the emulsifier-free emulsion polymerization experiments, potassium persulphate (KPS) was used as initiator and toluene as porogen whereas, for the single-step swelling and polymerization experiments, monodisperse polystyrene (PS) particles prepared by emulsion polymerization were used as seed particles, sodium dodecyl sulfate (SDS) and polyvinyl alcohol (PVA) as surfactants, azobisisobutyronitrile (AIBN) as initiator and toluene as porogen. The effect of the crosslinker concentration on the surface morphology of the polymeric nanoparticles was assessed by scanning electron microscopy. It was shown that, the pore size decreased by increasing the degree of crosslinking ($\bar{\nu}_c$) beyond a specific value (e.g., $\bar{\nu}_c > 16.5$ for particles prepared by emulsifier-free emulsion polymerization and 21.94 % for those prepared by a single-step swelling and polymerization process) and the particle surface exhibited an orange peel appearance. The pore size distribution of the particles was determined employing nitrogen adsorption/desorption. It was shown that for both types of particles (e.g., P(St/mDIB) and P(St/ β -CD), most of the pores had sizes in the range of 1 to 10 nm, while a small number of larger pores lied in the range of 10-50 nm. The adsorption efficiency of the polymeric nanoparticles in various pollutants (e.g., styrene, toluene, trihalomethanes, tri- and tetrachloroethylene) was determined employing a GC-FID method. Adsorption measurements with activated carbon (AC) were also performed for comparison purposes. The adsorption experiments were carried out in a batch mode. A fixed amount of particles was added to pollutant solutions of known concentration and kept under stirring for 24 hours. The Freundlich constant (KF) was calculated according to the initial and equilibrium liquid-phase concentrations, volume of the solution and mass of the adsorbent. It was shown that the polymeric nanoparticles have a low affinity for toluene and trihalomethanes, a moderate affinity for styrene and a high affinity for tri- and tetrachloroethylene higher than that of activated carbon. The porous nanoparticles were subsequently impregnated into ceramic carriers (e.g., SiC/TiO₂ (LiqTech, Denmark) and alumina (CTI S.A., France) filters with 52 channels and diameters equal to 25 mm), aiming to the formation of a highly-effective, hybrid water purification system which can remove organic contaminants at concentrations as low as a few ppbs. The polymeric nanoparticles were distributed rather homogeneously on the peripheral surface of the filters and a high percentage of coverage was achieved. A large number of particles could be found also inside the filter pores as revealed by the examination of the horizontal and vertical cross sections of the impregnated filters. The adsorption efficiency of the

hybrid filters was examined by HPLC at IWGA-SIG (Austria). It was shown that a SiC/TiO₂ filter impregnated with P(St/mDIB) nanoparticles with $\tilde{n}_c = 32.91\%$ performed very well with tetrachloroethylene. More specifically, the hybrid filter was found to retain 70-80% of the pollutant from a CCl₄ solution with concentration 100ppb whereas the SiC/TiO₂ filter retained only 45% of the pollutant under the same experimental conditions. The present study revealed that porous P(St/âCD) and P(St/mDIB) nanoparticles can be successfully prepared by emulsifier-free emulsion polymerization and a single-step swelling and polymerization process. The particles thus prepared were found to have a high affinity for specific organic pollutants present in potable water, higher than that of activated carbon, and were successfully impregnated in ceramic carriers resulting in the production of highly efficient hybrid filters for water purification.