Chemosphere 156 (2016) 302–311

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Use of hybrid composite particles prepared using alkoxysilane-functionalized amphiphilic polymer precursors for simultaneous removal of various pollutants from water

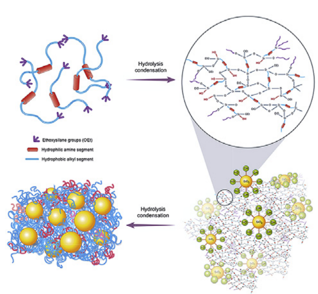
Seulki Cho [a, 1], Nahae Kim [b, 1], Soonjae Lee [c, 1], Hoseok Lee [b], Sang-Hyup Lee [a, d], Juyoung Kim [b, *], Jae-Woo Choi [a, e, **]

[a] Center for Water Resource Cycle Research, Korea Institute of Science and Technology, Hwarangno 14-gil 5, Seongbuk-gu, Seoul 136-791, Republic of Korea
[b] Department of Advanced Materials Engineering, Kangwon National University, Samcheok 245-711, Republic of Korea
[c] Department of Earth and Environmental Sciences, Korea University, Seoul 136-701, Republic of Korea
[d] Graduate School of Convergence Green Technology and Policy, Korea University, Seoul 136-701, Republic of Korea
[e] Department of Energy and Environmental Engineering, University of Science and Technology (UST), Daejeon 305-350, Republic of Korea

HIGHLIGHTS

- We present a new organic-inorganic hybrid particles as an adsorbent.
- Hyperbranch-like amphiphilic polymers is conjugated onto silica nanoparticles.
- The particle removed phenolic compound and azo dye from aqueous solution.
- The particle was easily separated type the treated water due to density difference.
- The particle is a promising sorbent for hydrophilic and/or hydrophobic pollutants.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 29 November 2015
Received in revised form
3 April 2016
Accepted 3 May 2016
Available online 12 May 2016

Handling Editor: Xiangru Zhang

Keywords:
Organic-inorganic hybrid particle

ABSTRACT

In this study, we present new inorganic-organic hybrid particles and their possible application as an adsorbent for simultaneous removal of hydrophobic and hydrophilic pollutants from water. These hybrid particles were prepared using tailor-made alkoxysilane-functionalized amphiphilic polymer precursors (M-APAS), which have amphiphilic polymers and reactive alkoxysilane groups attached to the same backbone. Through a single conventional sol-gel process, the polymerization of M-APAS and the chemical conjugation of M-APAS onto silica nanoparticles was simultaneous, resulting in the formation of hybrid particles (M-APAS-SiO_2) comprised of hyperbranch-like amphiphilic polymers bonded onto silica nanoparticles with a relatively high grafting efficiency. A test for the adsorption of water-soluble dye (organe-16) and water insoluble dye (solvent blue-35) onto the hybrid particles was performed to evaluate the possibility of adsorbing hydrophilic and hydrophobic compound within the same particle.

* Corresponding author. Department of Advanced Materials Engineering, Kangwon National University, Samcheok 245-711, Republic of Korea
** Corresponding author. Center for Water Resource Cycle Research, Korea Institute of Science and Technology, Hwarangno 14-gil 5, Seongbuk-gu, Seoul 136-791, Republic of Korea.
E-mail addresses: juyoungk@kangwon.ac.kr (J. Kim), plead36@kist.re.kr (J.-W. Choi).
[1] These authors contributed equally.

http://dx.doi.org/10.1016/j.chemosphere.2016.05.004
0045-6535/

Adsorption
Amphiphilic polymer
Density separation
Alkoxysilane

The hybrid particle was also evaluated as an adsorbent for the removal of contaminated water containing various pollutants by wastewater treatment test. The hybrid particle could remove phenolic compounds from wastewater and the azo dye reactive orange-16 from aqueous solutions, and it was easily separated from the treated wastewater because of the different densities involved. These results demonstrate that the hybrid particles are a promising sorbent for hydrophilic and/or hydrophobic pollutants in water.

1. Introduction

Various methods—such as ion exchange, neutralization, reverse osmosis, precipitation, solvent extraction, and adsorption—have been used for the removal of toxic compounds from aqueous solutions (Cai et al., 2014; Choi et al., 2011; Floch and Hideg, 2004; Juttner et al., 2000; Lin and Juang, 2009; Ozbelge et al., 2002). Among these methods, adsorption is considered an economical process because it is easy to implement and highly efficient in removing toxic compounds from aqueous solutions, especially at relatively low pollutant concentrations (Chung et al., 2014).

In fact, a number of adsorbents are used for the removal of heavy metals from aqueous solutions; these include activated carbon, modified clays, biosorbents, polymeric resins, zeolites, and hybrid materials (Jin et al., 2011; Qu et al., 2013; Samiey et al., 2014; Zhao et al., 2011). Recently, nano-sized particles such as surfactant micelles, amphiphilic polymer micelles, hyperbranched polymer nanoparticles, and cyclodextrin nanoparticles have been used for the removal of hydrophilic or hydrophobic pollutants from water phase (Juttner et al., 2000; Zhao et al., 2011). Under a low dosage, these nanoparticles boast very high adsorption capacities because of their extremely high surface areas (Zhao et al., 2011). Moreover, these nanoparticles all share a common self-assembled nanostructure, which consists of a hydrophobic core that encapsulates hydrophobic pollutants, along with an outer hydrophilic shell that adsorbs water-soluble dyes and metal ions (Zhao et al., 2011).

Despite the high adsorption capacity of these nano-sized adsorbents, applying them in the field is difficult because they cannot be fully separated and recovered after the treatment process has been completed (Jin et al., 2011; Qu et al., 2013; Samiey et al., 2014). Therefore, to avoid this fatal drawback, amphiphilic molecules (surfactants and amphiphilic polymers), dendrimers, and hyperbranched polymers are chemically bonded onto inorganic materials such as porous silica particles, titanium dioxide filters, or metal oxide membranes (Jin et al., 2011; Kango et al., 2013; Park et al., 2010; Qu et al., 2013; Rozenberg and Tenne, 2008; Samiey et al., 2014; Shin et al., 2008). However, the conjugation efficiency of the above-mentioned organic molecules onto inorganic materials is very low using conventional grafting processes. Accordingly, very complicated grafting processes, such as atom-transfer radical polymerization (ATRP) or reversible addition-fragmentation chain transfer (RAFT), must be employed to obtain acceptable grafting efficiencies (Park et al., 2010; Rozenberg and Tenne, 2008). However, ATRP significantly increases the cost of the process, thereby hindering its application in environmental remediation processes. In addition, hyperbranched polymers and amphiphilic polymers (in which functional groups react with surface functional groups of inorganic materials) are quite costly and could not be mass-produced, which makes these materials inappropriate for use in large-scale environmental processes (Jin et al., 2011). Therefore, a continual need exists for the development of a new adsorbent.

In recent years, it has been reported that organic-inorganic hybrid materials that are prepared using various organo-alkoxysilane compounds could function as promising adsorbents for the removal of pollutants from water (Jin et al., 2011; Liu et al., 2010; Samiey et al., 2014). Through simple sol-gel synthetic processes, particles or membranes for which organic and inorganic components are chemically bonded and mixed at the nano-scale can be formed (Kango et al., 2013; Samiey et al., 2014; Sanchez et al., 2010). However, in most cases, such particles and membranes exhibit impressive adsorption performance only for the removal of heavy metal ions from aqueous solutions or wastewater (Samiey et al., 2014). In fact, there are very few reports on hybrid materials that can adsorb hydrophobic pollutants and water-soluble pollutants simultaneously; this is because organo-alkoxysilane compounds with amphiphilic moieties are neither common nor commercially available.

In this study, we present the synthesis of organic-inorganic hybrid particles using alkoxysilane-functionalized amphiphilic polymer precursors, which have amphiphilic polymers and reactive alkoxysilane groups attached to the same backbone. Through a single conventional sol-gel process, an organic-inorganic hybrid composed of crosslinked amphiphilic polymers and siloxane networks can be formed. At the same time, the conjugation of hyperbranch-like amphiphilic polymers onto silica nanoparticles can be achieved with a relatively high grafting efficiency. Because the prepared organic-inorganic hybrid composite particles have charged hydrophilic moiety as well as a hydrophobic segment, the hybrid composite particles would be expected to be able to adsorb metal ions and hydrophobic pollutants simultaneously from water. In addition, inorganic components in the particles could provide chemical and physical stability and facilitate the recovery of the particles from water phase after the completion of the water treatment process.

2. Materials and methods

2.1. Chemicals and materials

In the synthesis of alkoxysilane-functionalized amphiphilic precursors (M-APAS), isophorone diisocyanate (IPDI, Junsei Chemical Co.), N-methyldiethanol-amine (MDEA, Aldrich Chemical Co.), and (3-aminopropyl) triethoxysilane (APTES, Aldrich Chemical Co.) were used as received. Dibutyltin dilaurate (DBTDL, Aldrich Chemical Co.) was used as a catalyst in the precursor synthesis. Silica nanoparticles (Aerosil 200) used in the synthesis of organic-inorganic composite particles were purchased from Evonik and were dried under reduced pressure for 1 d at 80 °C before being used. In addition, the azo dye reactive orange-16 was purchased from Sigma-Aldrich, Korea.

2.2. Synthesis of alkoxysilane-functionalized amphiphilic precursors

Alkoxysilane-functionalized amphiphilic precursors, M-APAS, were synthesized using a two-step reaction procedure. Schematic presentation for the reaction procedure and expected molecular structure of M-APAS are shown in Fig. 1. Molar ratio of all reactants