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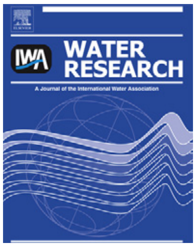

Surfactant-coated aluminum hydroxide for the rapid removal and biodegradation of hydrophobic organic pollutants in water

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ABSTRACT

The removal of hydrophobic organic pollutants in water to surfactant-coated aluminum hydroxide [surfactant-$Al(OH)_3$] was investigated. Anionic surfactants such as sodium dodecyl sulfate (SDS), sodium bis(2-ethylhexyl)sulfosuccinate (AOT), and sodium oleate were sorbed on positively charged aluminum hydroxide at pH 7 and formed hydrophobic aggregates that can incorporate hydrophobic organic pollutants in water. Because of the hydrophobic interaction and decrease in the positive charge, surfactant-$Al(OH)_3$ was coagulated into precipitates that can readily be separated from water. Hydrophobic organic pollutants such as alkylphenols, polycyclic aromatic hydrocarbons, estrogens, chlorinated antifungals, and pesticides were well collected to the precipitates and thus efficiently removed from water. The collection of hydrophobic organic pollutants was correlated to their aqueous-octanol distribution coefficient. The decomposition of hydrophobic organic pollutants was examined using a bacterial agent (*Bacillus subtilis*). Hydrophobic organic compounds collected to AOT-$Al(OH)_3$ or sodium oleate-$Al(OH)_3$ were insufficiently decomposed. On the other hand, nonylphenol, octylphenol, and pendimethalin collected to SDS-$Al(OH)_3$ were decomposed within 1 week. The decomposition was accelerated by the collection to SDS-$Al(OH)_3$.

1. Introduction

Hydrophobic organic pollutants such as alkylphenols, chlorophenols, pesticides, and polycyclic aromatic hydrocarbons are ubiquitous environmental pollutants resulting from waste from paper mills, sewage treatment processes, preparation of agricultural and industrial chemicals, and the combustion of fossil fuels. Because of their hydrophobic properties, these compounds tend to bioaccumulate in the lipid stores of animals and human beings. The potentials for several physiological actions including carcinogenic, mutagenic, estrogen-like properties have been reported (Laws et al., 2000; Ohe et al., 2004). Additionally, their fungicidal property potentially gives significant damages to the ecosystems involving bacteria and phytoplankton (Pelletier et al., 2006; DeLorenzo and Fleming, 2008). Methods for the efficient removal of such hydrophobic organic pollutants are required.

Among numerous water treatment techniques, the coagulation–sedimentation method is one of the most popular methods because of its simplicity, low cost, and easiness of scaling-up (Koening, 1967; Thébault et al., 1981; Randtke and Stephen, 1988). The method includes the addition of metal salt such as polyaluminum chloride or aluminum sulfate and the subsequent neutralization of water for the formation of

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aluminum hydroxide. Polymer flocculants such as sodium polyacrylate or sodium alginate are often used for facilitating the coagulation of finely dispersed aluminum hydroxide. The resulting flocks or precipitates can rapidly be separated by filtration. Particulate materials, colorized materials, and heavy metal ions are coprecipitated and efficiently removed from water. However, the removal of uncharged hydrophobic organic pollutants is often insufficient (Thébault et al., 1981; Boyd et al., 2003; Carballa et al., 2004; Suarez et al., 2009).

We have designed a simple and efficient method for collecting hydrophobic organic compounds in water using surfactant-coated solid materials (Hiraide et al., 1997; Saitoh et al., 2002a; Saitoh et al., 2004; Saitoh et al., 2005; Saitoh et al., 2005; Saitoh et al., 2007a). The method is based on the extraction of hydrophobic compounds to the surfactant aggregates (namely hemimicelles or admicelles) on the solid surfaces (Valsaraj, 1989, 1992; Sandeep et al., 1994). Several types of admicelles can be readily prepared only by mixing solid materials and appropriate surfactants in the aqueous solution. Hydrophobic organic compounds and metal chelates were well collected and highly concentrated to the admicelles. Due to high water-permeability of the admicelles, the solute incorporation was quite rapid comparing with the collection to conventional hydrophobic solid sorbents. Therefore, the admicelle-mediated separation technique has been extensively applied to preconcentrate varieties of hydrophobic organic compounds for their instrumental analyses (Merino et al., 2003; Costi et al., 2008; Moral et al., 2008; Gangula et al., 2010).

In the present study, we attempted the introduction of the admicelle-mediated separation methodology to the coagulation and sedimentation technique. Since aluminum hydroxide is positively charged at neutral pHs, anionic surfactants added are expected to be sorbed on the aluminum hydroxide to form surfactant-coated aluminum hydroxide [surfactant-$Al(OH)_3$]. The anionic surfactant molecules can aggregate and provide hydrophobic media for the incorporation of hydrophobic organic pollutants. The potential usefulness of surfactant-$Al(OH)_3$ for rapid and efficient removal of different hydrophobic organic compounds in water was investigated. Furthermore, biodegradation of hydrophobic organic pollutants was examined using bacteria that can be activated in the presence of anionic surfactant.

2. Meterials and methods

2.1. *Apparatus*

An HPLC system composing of a Jasco (Tokyo, Japan) PU-980 intelligent pump, a UV-970 intelligent ultra-violet detector, and an 807-IT integrator were used for the separation and determination of hydrophobic organic pollutants. Zeta-potential of surfactant-$Al(OH)_3$ was measured with a Microtec Nition Zeecom ZC2000 zeta-potential analyzer (Tokyo, Japan). A Jasco 4200 FT-IR spectrometer (Hachioji, Japan) was used for the FT-IR analysis of surfactant-$Al(OH)_3$. Fluorescence spectra were measured with a Perkin–Elmer LS-50B luminescence spectrometer (Waltham, MA, USA) with a 1 cm quartz cell. Purified water was prepared with Elix UV3 and Milli-Q Gradient A10 Water Purification Systems having a UV irradiation component (Millipore, Milford, MA, USA). A rotary shaker incubator (120 rpm, MMS-310 and FMC-1000, Tokyo Rikakikai, Tokyo, Japan) was used for the experiments of biodegradation. Dissolved oxygen was monitored with a Toa MM60R water quality meter (Tokyo, Japan). A Branson Model 450 sonifier (output control 1, Danbury, CT, USA) was employed to facilitate the elution of hydrophobic organic pollutants.

2.2. *Materials*

An Al(III) solution (50 g L^{-1} as Al(III) ions) was prepared by dissolving aluminum(III) chloride hexahydrate with water. Sodium dodecyl sulfate (SDS, for biochemical, Wako Pure Chemical, Tokyo, Japan), sodium bis(2-ethylhexyl)sulfosuccinate (AOT, Docusate™ sodium salt, Sigma–Aldrich, St. Louis, MO, USA), and sodium oleate (Tokyo Chemical, Tokyo, Japan) were used as 50 g L^{-1} aqueous solutions. Benz[a]anthracene, benzo[a]pyrene, fluoranthene, pyrene, estrone, β-estradiol, esprocarb, methoxychlor, pendimethalin, pretilachlor, 4-*n*-octylphenol, 4-*n*-nonylphenol, 3,4,4-trichlorocarbanilide (triclocarban), and 2,4,4′-trichloro-2′-hydroxydiphenyl ether (triclosan) were obtained from Wako Pure Chemical. They were employed as 1 g L^{-1} ethanol solution. A molecular probe, *N*-phenyl-1-naphthylamine (PN, Wako Pure Chemical) was used as 1 mM ethanol solution. A bacterial agent, DT-5045 (*Bacillus subtilis* for the degradation of oil, tar, aromatic hydrocarbons, and phenols Dyna-Bio-Cultures, Environmental Dynamics Inc., Columbia, MO, USA), was supplied by Sanyugiken (Shiki, Japan). Other chemicals employed were of analytical grade.

2.3. *Removal of hydrophobic organic pollutants*

To 100 mL of water containing prescribed amount of hydrophobic organic pollutants was added 200 μL of Al(III) solution. With vigorous stirring, the solution pH was adjusted to 7 by the careful addition of 4 M sodium hydroxide solution using a micropipette. It was further stirred for 15 min in order to ensure the complete formation of aluminum hydroxide. Then, the prescribed amount of surfactant solution was added to the suspension. After stirring the mixture for 15 min, the formed precipitates were separated by centrifuging the solution at 1500 rpm (300 g) for 5 min. Hydrophobic organic pollutants remaining in the supernatant were determined by introducing 20 μL-aliquot of the supernatant to the HPLC system.

2.4. *Characterization of surfactant-$Al(OH)_3$*

The amount of surfactant sorbed on aluminum hydroxide was estimated from the surfactant concentration in the bulk aqueous solution which was spectrophotometrically determined by a methylene blue method (Longwell and Maniece, 1955). For FT-IR analysis, surfactant-$Al(OH)_3$ formed was collected by filtration and was freeze-dried for 72 h. It was well mixed with KBr (1:100) and pressed into the disk. For the evaluation of the hydrophobic properties of surfactant-$Al(OH)_3$, it was prepared from 0.25 mM Al(III) and 1 mM surfactant. A 10-μL portion of PN solution was added to 10 mL of surfactant-$Al(OH)_3$ solution. The emission of PN in the different surfactant-$Al(OH)_3$ systems was measured. The wavelength of the excitation was 340 nm.