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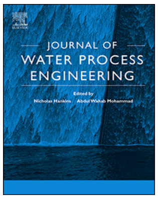

TiO_2-PDMS composite sponge for adsorption and solar mediated photodegradation of dye pollutants

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ABSTRACT

A hydrophobic composite sponge with photocatalytic property is fabricated combining porous polydimethylsiloxane (PDMS) structure and semiconductor TiO_2 nanocatalyst. The porous PDMS structures are prepared using sugar as a sacrificial template. The typical size of the pores in the sponge varies from 10 µm to 100 µm. The surface and the pore wall of the PDMS sponge are decorated with TiO_2 nanoparticles which are mostly present as an aggregate. These PDMS composite sponges were shown to remove organic pollutants such as the toxic dye Rhodamine B from water efficiently and selectively, via synergistic effects of adsorption and photocatalytic degradation. These sponges first remove a significant amount of the dye from solution by adsorption (~50% removal) even in the absence of light. Upon exposure to solar light, the dye adsorbed on the surface of the TiO_2-PDMS sponge was photocatalytically degraded, resulting in the further removal of the dye from solution (total 80% removal). The overall dye removal efficiency TiO_2-PDMS composite sponge is comparable with that of a similar amount of the TiO_2 in solution. However, the application of composites eliminates the need for complicated separation of the powder catalyst from the solution. Most importantly these composite sponges could be easily regenerated by exposing them to solar light. The excellent performance and the recyclability of these cost-effective TiO_2-PDMS sponges suggest their promising applications in textile wastewater treatment.

1. Introduction

Contamination of water sources and shortages of clean, drinkable water is a serious problem globally [1–3]. Various efforts are being made to provide clean water, as well as to remove contaminants from wastewater sources to mitigate environmental damages. Textile wastewater containing significant amount of synthetic dyes poses serious threat to marine environments [4–6]. Azo dyes, which constitute up to 70% of the total textile dyes, are recalcitrant, non-biodegradable, and persistent, and their transformation products, aromatic amines, are usually toxic to aquatic organisms [7,8]. Additionally, the textile industry has an inherently high-water consumption and wastewater discharge rate, which contains a significant amount of the dye. Unfortunately, most of the existing techniques for the removal of azo dye suffer from various drawbacks. Removal of dye using activated carbon involves only the phase transfer of pollutants which requires an additional treatment process [9]. Application of membrane to remove azo dyes leads to secondary waste effluents and suffers from membrane fouling and flux decline. Biological treatments require strict controls over pH and temperature [10]

Photocatalysis has been demonstrated as a low-cost and sustainable technology for the photocatalytic degradation of azo dyes [11–13]. One of the main advantages of the photocatalysts is the utilization of solar energy to decompose the organic pollutants. An example is the application of a TiO_2-based photocatalytic system for the degradation of pollutants from air and water under solar light. Titanium dioxide is identified as one of the most efficient photocatalysts for the water pollutants because of its photostability, low cost, and resistance to corrosion [14–16]. However, owing to the short wavelength cutoff of TiO_2 adsorption, only a small fraction of solar photons (~4%) can be utilized to excite this photocatalyst, resulting in a low photocatalytic yield [17]. The separation process of the TiO_2 nanoparticles from the treated water causes additional complexity [17,18]. Free TiO_2 nanoparticles left in water have been shown to be harmful to aquatic organisms [18–20]. This problem can be eliminated by immobilizing the photocatalyst on a substrate or integrated into thin films or polymers [21–23].

To date, a wide range of materials, such as polymer films, porous polymers have been used to immobilize TiO_2 [23–25]. For example, TiO_2 is utilized in nanocomposite coatings to produce self-cleaning

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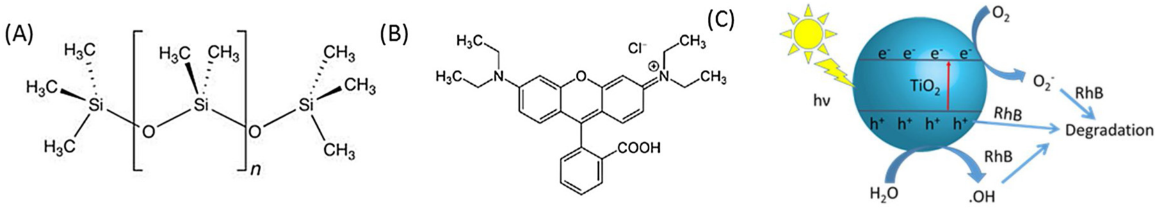

Fig. 1. Chemical structure of (A) PDMS (B) Rhodamine B (C) Schematic of Rhodamine B (RhB) degradation by TiO_2 in the presence of sunlight.

surfaces, as well as to produce catalytic membranes for creating fabrics capable of oil-water separation, pattern printing, and super hydrophobicity [14,21,25,26]. By incorporating the catalyst into a porous, hydrophobic substrate, water treatment can be accomplished by both photocatalysis and physical separation of the contaminant from the water. However, challenges remain in developing large-scale non-toxic photocatalyst polymer composites in an inexpensive and efficient way. Most of the methods reported in the literature include complicated synthesis method or expensive ingredients [21,25,27].

Here, we present a high-performance, reusable composite incorporating a photocatalyst like TiO_2 onto PDMS sponges for removal and solar-mediated degradation of toxic azo dye Rhodamine B from the water. PDMS consists of repeated units of -$OSi(CH_3)_2O$- and is inherently hydrophobic. It is known for its ability to absorb small hydrophobic molecules and organic molecules. PDMS will absorb Rhodamine B molecule through its nonpolar hydrophobic end (Fig. 1(A) and (B)). PDMS is routinely used as a biomedical implant material and for fundamental cellular studies and has been confirmed as a biocompatible material [28,29]. Similarly, the biocompatibility of TiO_2 nanoparticles is researched due to its increased application in everyday life [18]. However, the biocompatibility of TiO_2 may not be an issue for the current application since TiO_2 is immobilized in the PDMS sponge matrix. Furthermore, the strong adhesion of TiO_2 with the PDMS is ensured to prevent their leaching from PDMS to the environment. The price of raw material for PDMS is comparable with other polymeric membrane materials such as cellulose acetate and polyvinylidene fluoride (PVDF). It can be cheaper than many other commonly used polymers for wastewater treatment such as an anionic perfluorinated polymer (Nafion), cellulose acetate, polycarbonate (PC), polysulfone fluoride (PSF) [30]. Moreover, unlike many other membranes, the preparation of the PDMS sponge does not require any expensive chemicals or intricate synthesis processes or equipment. This cost-effective and biocompatible material is readily adapted to making porous, sponge-like structures [31,32]. PDMS sponges have been shown to be capable of selectively absorbing oils and organic solvents and heavy metal ions from water [33–36]. PDMS possess high transmittance and low adsorption under solar light, which is suitable for desirable photo mediated applications [37]. Porous PDMS can also be compressed repeatedly without losing structural integrity, meaning it can be easily recycled and used in applications that require fitting in complex geometries.

For the first time, we have demonstrated the application of a TiO_2-PDMS composite sponge which cannot only efficiently remove organic compounds from wastewater by adsorption but also by subsequently breaking them down via the photocatalytic action of TiO_2 under solar light (1(C)). Most importantly, owing to the photocatalytic effect of TiO_2 the TiO_2/PDMS sponge can be easily regenerated by exposing them to solar light. The PDMS sponges were prepared using a simple sugar template method. The sugar was leached using water. The surface-modified TiO_2 was added to PDMS sponge by a simple injection method. This technique is suitable for scaled-up production [32]. This study focused on dye removal from water as a function of the amount of TiO_2 in the PDMS sponge versus the initial concentration of the dye. It has been demonstrated that these sponges can be recycled at least three times without losing efficiency.

2. Materials and methods

2.1. Fabrication of composite sponge

Titanium dioxide (TiO_2) nanopowder (Aeroxide® P25) was purchased from Sigma-Aldrich. According to the manufacturer's data, the TiO_2 has a specific surface area of 35–65 m^2/g (BET) and a mean diameter of 21 nm. PDMS prepolymer (Sylgard 184A) and the thermal curing agent (Sylgard 184B) were purchased from Galco Industrial Electronics. The PDMS sponges were fabricated following a method mentioned in the literature [36]. Briefly, commercially available cube sugar was used as a template to fabricate porous PDMS. Initially, standard sugar cubes were dipped in a 10:1 ratio solution of PDMS prepolymer and a curing agent. The cubes were then placed under vacuum for degassing. The polymer mixture infiltrated into the intergranular spaces of the sugar templates due to capillary forces. The sugar template with absorbed polymer solution was placed in an oven at 70 °C for 1 h to complete the curing process. The cured polymer-sugar template sponges were then immersed in warm (75–80 °C) water to leach out the sugar, leaving the final PDMS sponge structures.

A 1 mg/ml solution of titanium dioxide was prepared in a solution of hexamethyldisiloxane (HMDS) and ethanol (1:10 by volume). Different amounts of TiO_2 solution were injected into the PDMS sponges to achieve TiO_2-PDMS sponge composites with different concentrations of TiO_2. The residual ethanol in the sponges was allowed to evaporate at room temperature. TiO_2-PDMS composite sponges were prepared with three different concentrations of catalyst: 36 μg/gm of sponge, 71 μg/gm of sponge, and 142 μg/gm of sponge.

2.2. Characterization of TiO_2-PDMS composite sponge

The TiO_2-PDMS sponges were characterized using a Thermo Scientific Evolution™ 300 UV–vis Spectrophotometer equipped with the integrated sphere. Structural characterization of the composite was performed using a Hitachi S-3200N scanning electron microscope. Energy dispersive X-ray spectroscopy (EDX) was performed using the same microscope to confirm the composition of the composite sponges.

2.3. Photodegradation experiments

Rhodamine B was used as a model azo dye to assess the effectiveness of the sponges in removing dye from water. TiO_2-PDMS composite sponges were cut into thin slices (2–3 mm) to allow for light adsorption. The composite sponges were immersed in 6 ml of different concentration Rhodamine B solutions. Before irradiation, the dye solution containing the sponge sample was kept in the dark overnight to allow the dye adsorption by the sponge to reach equilibrium. After this, the dye solution with a sponge, in a quartz tube, was exposed to the solar spectrum at an intensity of 100 mW/cm^2. For solar light, an ABET Technologies SunLite™ solar simulator with AM 1.5 filter and a 1000 W xenon arc lamp were used. The samples were exposed to solar light for 1 h. Aliquots of dye solution were collected in 10 or 15-min increments, and the concentration of dye in the solution was monitored by UV–vis spectroscopy.