Peat moss-derived biochar for sonocatalytic applications

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ABSTRACT

Peat-moss derived biochar was used as a sonocatalyst for the degradation of rhodamine B (RhB) at different ultrasonic frequencies (40 kHz and 300 kHz). The biochar was prepared by pyrolysis of peat-moss at 300 °C under N_2-saturated conditions. High removal efficiency was achieved when biochar (1000 mg L^{-1}) was used as a sonocatalyst in the 40 kHz system, and high removal could be achieved by pre-adsorption and radical oxidation reactions on the surface of the biochar. This was validated in experiments employing radical scavengers. Sonochemiluminescence images and real images of the systems with no biochar, 100 mg L^{-1} biochar, and 1000 mg L^{-1} biochar also supported this observation. On the other hand, the addition of the biochar was less effective than expected for the degradation of RhB at 300 kHz. This was due to low dispersion of the biochar in solution in the high frequency system, where relatively weaker sonophysical effects could be obtained.

1. Introduction

Among the diverse advanced oxidation processes, the sonochemical process provides unique physical and chemical phenomena for the removal of organic contaminants from various media. Depending on the physical and chemical properties of the target contaminants, degradation during the sonochemical process proceeds by different chemical mechanisms, including pyrolysis inside a cavitation bubble or in the interfacial region of a cavitation bubble, and radical redox reactions in the bulk solution. In addition, physical effects such as microjets, microstreaming, and shockwaves also aid degradation by facilitating mass transport [1–4]. However, the sonication process requires a large amount of energy to achieve adequate degradation efficiency [5]. To solve this problem, the synthesis and application of various catalysts have been attempted [6–9].

Two different mechanisms have been proposed to explain the sonocatalytic enhancement. One is the increase in the bubble number, provided by a solid surface that reduces the nucleation threshold. The physical and chemical properties of the solid particles are strongly related to nucleation of the cavitation bubbles, which significantly affects the resulting sonocatalytic activity. The second mechanism occurs when the catalyst is a semiconductor, and the catalyst is activated by light and heat emitted from the cavitation bubble [9–11]. TiO$_2$, which is a common photocatalyst, can be activated by irradiation in the

ultraviolet (UV) range (< 400 nm) or by heat energy (> 500 °C), producing electron-hole pairs; this process results in the generation of radical species for oxidation and reduction of the target contaminants. Because the wavelength of light emitted by a cavitation event spans the UV and visible spectral regions, and the internal temperature of the bubble reaches over 5000 K, cavitation events can provide sufficient energy to activate a semiconductor catalyst [12]. Unfortunately, it is not easy to distinguish between the two mechanisms for semiconductor catalysts, because the nucleation mechanism is also operative with semiconductor materials. Therefore, the bubble nucleation mechanism should be first investigated by using non-semiconducting materials, and the photo- and thermal-excitation mechanisms should then be investigated using semiconducting materials to achieve enhancement of both cavitation mechanisms.

Biochar is a carbon-enriched material produced by the pyrolysis of biomass under oxygen-limited conditions. Because biochar has a high specific surface area and porous structure, it has been used as an economic adsorbent for the removal of organic and inorganic pollutants from various systems [13]. Furthermore, the facile mass production of biochar makes it potentially feasible for environmental application. Recently, biochar obtained from food wastes such as orange peel, sugar cane bagasse, and spent coffee grounds has gained popularity as an effective adsorbent for emerging aqueous pollutants [14–16].

The relatively high specific surface area and hydrophobic

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characteristics of micro/nano-sized particles can accelerate cavitation bubble nucleation in sonocatalytic systems. One of the well-known mechanisms by which this occurs is the reduction of the threshold energy for microbubble formation [17]. Furthermore, gases entrapped in the micropore and mesopore channels have the potential to form cavitation bubbles after escaping from the pores and reaching the particle surface or the bulk solution [18]. Due to the relatively simple mechanism of operation of non-semiconducting catalysts compared to semiconducting catalysts, it is more convenient to explore the mechanisms of removal of target analytes using the former material in a sonocatalytic system.

The effect of ultrasound on adsorption processes using activated carbon and biochar under various frequency conditions has previously been explored, revealing that the presence of carbon particles in an aqueous phase could significantly enhance the adsorption and degradation of various pollutants due to ultrasound-induced surface activation and sonocatalytic enhancement [6,19–21]. Thus, it is proposed that micro/nano-sized carbon particles such as food waste-derived biochars may useful for enhancing cavitational effects.

In a preliminary test, we observed a similar enhancement of sonochemical oxidation reactions for sonocatalytic systems using spent coffee powder and peat moss-derived biochar. Therefore, the purpose of this study is to investigate the effect of peat moss-derived biochar in the sonocatalytic degradation of rhodamine B (RhB), as a model organic pollutant, under different ultrasonic frequency conditions. The role of biochar in the sonocatalytic processes is analyzed using degradation tests and radical scavenger tests at 40 kHz and 300 kHz. The results obtained in this study are also validated based on sonochemiluminescence (SCL) images.

2. Materials and methods

2.1. Chemicals

Canadian sphagnum peat moss (Lambert the Black Bale™, Canada) was used as the starting material for pyrolyzed biochar. Rhodamine B ($\geq$ 95% purity), tert-butyl alcohol ($\geq$ 99% purity, t-BuOH), and luminol (3-aminophthalhydrazide) were purchased from Sigma-Aldrich and used without further purification. Degussa P25 TiO_2 (Evonik, Germany) was used as a reference sonocatalyst for comparison with biochar.

2.2. Preparation of biochar

The biochar was prepared by a previously described process [22]. Briefly, 140 g of commercial Canadian sphagnum peat moss was placed in a stainless steel gas-tight cylindrical reactor (diameter: 50 mm, length: 300 mm). A flow of N_2 gas (100 mL min^{-1}) was used to purge the system for 2 h at 100 °C to remove oxygen and moisture in the column. The temperature was then increased to 300 °C at a rate of 7.58 ± 0.69 °C min^{-1} and held for 2 h at the desired temperature. The reactor was cooled for 3 h at room temperature (25 °C) under flowing N_2 gas to obtain biochar pyrolyzed at 300 °C. The measured Brunauer-Emmett-Teller (BET) specific surface area was 53.5 m^2 g^{-1}, which is similar to that of the commercial TiO_2 used for reference.

2.3. Sonochemical activity tests

The sonochemical activity tests were carried out with two different sonoreactors; namely, a 40 kHz ultrasonic bath (cleaner) and a 300 kHz cup-horn type sonicator. The experimental schemes were similar for both systems, as shown in Fig. 1. In the 40 kHz ultrasonic bath system equipped with a cooling system, 1 L of distilled water was used to fill the bath-type reactor, and a 100 mL beaker was submerged in the reactor. The temperature was maintained at 25 °C. Biochar (0.1 g) was added to 90 mL of water and magnetically stirred for 30 min at 1000 rpm. A 10 mL aliquot of RhB stock solution (100 mg L^{-1}) was
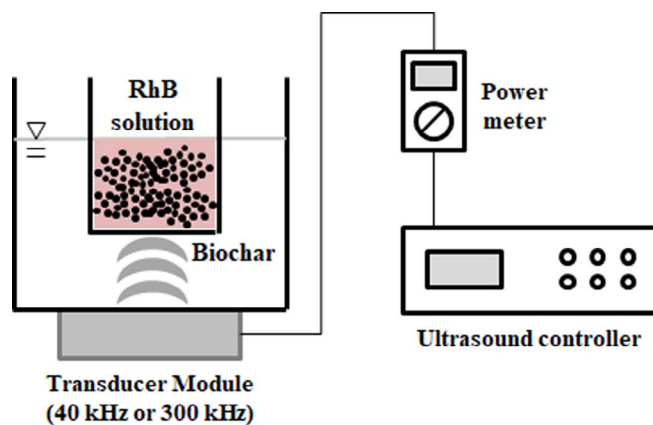

Fig. 1. Schematic of sonoreactors used for 40 kHz and 300 kHz experiments in this study.

added to the biochar suspension and continuously stirred for 10 min to produce a homogeneous solution. No mechanical mixing was applied during ultrasound irradiation to avoid changes in the sound energy field due to violent fluid movement in the sonoreactor. The prepared solution was submerged in the bath-type sonoreactor. The electrical input power was 35 W and the measured calorimetric power was 1.2 W (the calorimetric power density in the working volume was 12.3 W L^{-1}). The concentration of RhB was measured from the absorbance data at 554 nm using a UV–vis spectrophotometer.

In the 300 kHz cup-horn type reactor system equipped with a cooling system, 500 mL of distilled water was poured into the reactor and another reactor filled with 100 mL of solution was submerged in the cup-horn type reactor. The preparation, reaction procedure, and RhB concentration measurements were the same as used for the 40 kHz system. The electrical input power was 35 W and the measured calorimetric power was 2.8 W (the calorimetric power density in the working volume was 27.7 W L^{-1}).

Sonochemiluminescence (SCL) images were obtained using a luminol solution (0.1 g L^{-1} luminol (3-aminophthalhydrazide) and 1 g L^{-1} NaOH) in a completely dark room [2,3]. The exposure time used for the digital camera (Sony A58) was five minutes.

3. Results and discussion

3.1. Removal of RhB at 40 kHz

The changes in the concentration of RhB as a function of the sonication time are shown in Fig. 2. Before ultrasound irradiation, the mixture was stirred for 10 min to achieve homogenous dispersion of the biochar. The use of biochar in the 40 kHz sonochemical process led to a removal efficiency of 51.8% after sonication for 1 h. This removal efficiency is comparable to those reported in previous research [23–26]. This high removal ratio can be explained in terms of two possible mechanisms. The first is RhB adsorption on the surface of the biochar. Rapid sorption was observed during the 10 min preparation of the suspension, and the removal efficiency was around 14.6%. In the subsequent adsorption of RhB by biochar over the course of 1 h, only an additional 4.3% of RhB was removed. This means that most of the adsorption sites on the surface of the biochar were occupied by RhB molecules within a relatively short time. The specific surface area of the biochar (53.5 m^2 g^{-1}) used herein was quite low compared to that of commercially available activated carbon (1000–1200 m^2 g^{-1}). The other mechanism involves radical oxidation reactions induced by the acoustic cavitation events. The significant reduction in the removal efficiency upon addition of t-BuOH (Fig. 2) indicates that the main removal mechanism is oxidation by OH radicals generated during the cavitation events.

In the adsorption tests with and without t-BuOH, clear evidence of