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$BaTiO_3/TiO_2$ composite-assisted photocatalytic degradation for removal of acetaminophen from synthetic wastewater under UV–vis irradiation

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ABSTRACT

This study investigates the performance of $BaTiO_3$ and its composite with TiO_2 for photodegradation of acetaminophen (Ace) from synthetic wastewater. The morphology of the $BaTiO_3/TiO_2$ composite, acting as a photocatalyst, was characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and UV–vis absorption spectra techniques. The effects of operating parameters on the photo- degradation reaction and its degradation mechanisms were also investigated. The removal of Ace by photocatalytic degradation using $BaTiO_3/TiO_2$ composite was evaluated and compared to that of TiO_2 and $BaTiO_3$ alone in terms of dosage, initial concentration, reaction time, and pH. It was found that the performance of the $BaTiO_3/TiO_2$ composite as the photocatalyst in this study could be improved by varying the ratio of $BaTiO_3$ and TiO_2 dose. The $BaTiO_3/TiO_2$ ratio of 3:1 (w/w) was found to maximize the photodegradation of Ace. Under optimized conditions of 5 mg/L of Ace concentration, 1 g/L of $BaTiO_3/TiO_2$ composite, pH 7 and 4 h of reaction time, an Ace removal of 95% was attained. The result of photocatalytic degradation by the $BaTiO_3/TiO_2$ composite was significantly higher (95%) than that by the individual $BaTiO_3$ (18%) and TiO_2 (33%) alone under the same conditions. The oxidation by-products, resulting from this treatment, included hydroquinone and 1,4-benzoquinone. It is important to note that the treated effluents still could not meet the maximum limit of less than 0.2 mg/L set by the China's and the US' legislation. This suggests that subsequent treatment using biological processes is still required to complement the degradation of the target pollutant in the samples.

1. Introduction

In recent years one sixth of the world's population or almost 1.5 billion people living in developing countries lack access to safe drinking water, which has been considered as one of the most serious challenges to our well-being [1–3]. This situation worsens as water supply is contaminated by pollutants such as pharmaceuticals or endocrine-disrupting compounds (EDCs) from industrial sources. Pharmaceuticals and personal care products (PPCPs), which have attracted growing concerns worldwide, have been identified as emerging contaminants due to their potential impacts to public health [4]. Compared to conventional persistent organic pollutants (POPs) such as pesticides and polychlorinated biphenyls, PPCPs are unique in terms of their high polarity and low volatility.

As the world's most populous country, China has extensive production and consumption of PPCPs [5]. Among various PPCPs, acetaminophen (Ace) has been identified as one of the most widely application drugs since it is frequently used for relief of fever, analgesic pain and headache [6,7]. This substance is toxic when it is overdosed and is a primary cause of acute liver and kidney failure [8,9].

The threats posed to living organisms by the discharge of the toxic substances into the aquatic environment need to be considered carefully. After conventional treatment using biological processes, Ace is still detectable both in discharged wastewater and natural water bodies from diverse sources, like sewage treatment plants and surface water [10,11]. There is a growing concern regarding the implication of PPCPs discharged indirectly into the environment. So far, conventional physico-chemical treatment or biological process cannot remove these pollutants effectively [12]. Therefore, an alternative approach is required to address this particular problem.

In recent years a number of treatment methods have been developed and tested in laboratory systems or pilot plants to remove PPCPs from wastewater [13]. Among various methods, advanced oxidation process (AOPs), especially photocatalytic degradation, may be promising due to the generation of hydroxyl radicals (·OH), which could rapidly and indiscriminately degrade target pollutants in aqueous solution.

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Integrating AOP with UV light and a novel photocatalyst would accelerate the degradation of target pollutant through ·OH. The mechanism of photocatalytic degradation is mainly based on the electron-hole pair excited by light with energy greater than its band gap [14], where the light induces charge carriers to take a part in the oxidation reaction between target pollutants and the photocatalyst.

A variety of photocatalysts, like TiO_2, ZnO, ZnS and PbO_2 have been explored for their capability of breaking down organic pollutants. Among them, TiO_2 was the most commonly used photocatalyst due to its low-cost and low toxicity. However, the features of wide band gap and high recombination rate in TiO_2 often result in its low photocatalytic performance for removal of organic contaminants. In addition, TiO_2 has drawbacks such as low quantum yields and lack of visible-light utilization [15]. Consequently, a large number of UV lamps are required to maximize photodegradation of target pollutants in the liquid phase, thus increasing operational cost. This drawback limits the applications of UV/TiO_2 as practical remediation technology in larger scales. Therefore, the search for an alternative photocatalyst has been intensified recently to address this shortcoming.

Compared to TiO_2, $BaTiO_3$ is a perovskite semiconductor with a wide band gap coupled with a strong ferroelectric property. This unique property may enhance its catalytic activity during photocatalytic reactions, as this presents inherent chemical reactivity that makes it widely used for electronic applications [16,17]. Previous studies have demonstrated that $BaTiO_3$ could effectively remove methyl red [18], and RhodaminB [19,20]. Those preliminary studies indicate that $BaTiO_3$ is promising for photocatalytic reaction. Since the valence and the conduction band of the $BaTiO_3$ are higher than those of the TiO_2, a composite of $BaTiO_3$ and TiO_2 not only stimulates a rapid transfer of electron, but also generates additional holes between the former and the latter under UV–vis light irradiation.

A number of studies [16–18,21] have demonstrated that the use of $BaTiO_3$ for photocatalytic degradation could remove pollutants such as diclofop-methyl and dyes. According to Li et al. [16], the photodegradation of methylene blue (MB) by $BaTiO_3$ involved the generation of electrons in $BaTiO_3$ and holes in TiO_2, which then migrate to the conduction band in $BaTiO_3$ and the valence band in TiO_2, producing ·OH as a powerful oxidizing agent to degrade target molecules (Reactions Eqs. (1)–(6)).

$$BaTiO_3 \xrightarrow[hv]{} BaTiO_3(e_{cb}^- + h_{vb}^+) \quad (1)$$

$$e_{cb}^- + O_{2(adsorbed)} \rightarrow \cdot O_{2(adsorbed)}^- \quad (2)$$

$$e_{cb}^- + h_{vb}^+ \rightarrow heat \quad (3)$$

$$TiO_2 \xrightarrow[hv]{} TiO_2(e_{cb}^- + h_{vb}^+) \quad (4)$$

$$h_{vb}^+ + OH_{(surface)}^- \rightarrow \cdot OH \quad (5)$$

$$h_{vb}^+ + H_2O_{(adsorbed)} \rightarrow \cdot OH + H^+ \quad (6)$$

where hv is the UV radiation, while h_{vb}^+ and e_{cb}^- represent the valence-band holes and conduction-band electron respectively. The photogenerated valence band holes (h_{vb}^+) and conduction band electrons (e_{cb}^-) can either recombine to liberate heat (Reaction Eq. (3)) or make their ways to the surface of the photocatalyst, where they react with target species adsorbed at the solid-liquid interface.

As reflected by the Reactions (1–6), integrating the $BaTiO_3$ and TiO_2 as a composite that act as a photocatalyst with UV–vis irradiation may accelerate the degradation of target compound in solutions. Although previous studies have used $BaTiO_3$ to assist photodegradation process, most of the preparation process of the works involved multiple steps like hydrothermal, solvothermal and precipitation deposition [19]. So far, none has reported the technical feasibility of $BaTiO_3$/TiO_2 composite using one-step calcination for water treatment applications. Calcination is a thermal treatment conducted in the presence of air or nitrogen gas to heat the solid material, thus removing some volatile material like CO_2, water and organic material from the material without any fusion [22]. Compared to other preparation processes, one-step calcination method is a non-toxic, cost-effective and environmental friendly method without using any surfactants, additives or organic solvents.

With calcination, both $BaTiO_3$ and TiO_2 could be integrated into a composite that has unique physico-chemical properties, different from its starting materials, useful for promoting an effective photocatalytic degradation. Integrating TiO_2 photocatalyst with a wide band gap electron with another narrow band gap semiconductor may accelerate the transfer of photogenerated electrons in the composite photocatalysts [13]. This is the first reported study of coupling $BaTiO_3$ with TiO_2 using calcination method for photodegradation reaction of Ace under UV–vis light irradiation.

The laboratory study reported in this article investigates the removal of Ace by photocatalytic treatment using $BaTiO_3$/TiO_2 as a composite photocatalyst. To improve the Ace removal, different doses of $BaTiO_3$ and TiO_2 were varied under the same operating conditions. Other parameters including dosage, initial concentration, reaction time and pH were also optimized. The effects of operating parameters on the photodegradation reaction were also investigated. The Ace removal by the $BaTiO_3$/TiO_2 composite photocatalyst was evaluated and statistically compared with those of other previous studies.

2. Materials and methods

2.1. Materials

$BaTiO_3$ (99.9%) and TiO_2 (99%) in powder form were supplied by Sigma Aldrich (Saint Louis, USA). Acetaminophen was provided by Acros (New Jersey, USA) and used in its as-received form from the supplier without further purification. The characteristics of Ace are presented in Table 1. The pH of the solution was adjusted by 1.0 M NaOH and/or HCl and measured using a pH meter (Mettler FE 20, Switzerland). All of the standard solutions were freshly prepared from a

Tablet 1
Properties of acetaminophen.
Source: [23]

	Molecular formula	Molecular weight (g/mol)	λ_{max} (nm)	Structure
Acetaminophen	$C_8H_9NO_2$	151.16	243