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Preparation of bismuth titanate/calcium alginate composite bead and its photocatalytic degradation of dye pollutants

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Preparation of bismuth titanate/calcium alginate composite bead and its photocatalytic degradation of dye pollutants

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Abstract. In this study, the bismuth titanate/calcium alginate composite bead was synthesized by immobilizing bismuth titanate $Bi_4Ti_3O_{12}$ particles into 1.5% sodium alginate (SA) matrix. The $Bi_4Ti_3O_{12}$ particles were characterized by X-ray diffraction (XRD). The photocatalytic activity for the degradation of dye Rhodamine B in solution by as-prepared bismuth titanate/calcium alginate composite bead was investigated. The as-prepared composite beads CA/BTO-700 exhibited best photocatalytic efficiency for the degradation of RhB compared with CA/BTO-800 and CA/BTO-900 under simulated solar light. After 4 cycles in photocatalytic degradation of RhB, the degradation rate of the CA/BTO-700 nearly remained unchanged.

1. Introduction

In recent years, the application of photocatalysis for the decontamination of wastewaters has attracted enormous attention. Many efforts have been devoted to develop novel photocatalyst with high efficiency for environmental protection [1-2]. Bi(III)-containing oxides have become an exciting and growing area of research due to its excellent photocatalytic properties [3-4]. $Bi_4Ti_3O_{12}$ belongs to the layered Aurivillius oxide family and has been widely researched in the fields of electroceramics and piezoelectric materials [5]. Recently, $Bi_4Ti_3O_{12}$ has been explored as a visible-light photocatalyst with excellent photocatalytic activity for the removal of organic dyes and water splitting [6-7]. However, the suspended photocatalyst $Bi_4Ti_3O_{12}$ particles in the wastewater caused the secondary pollution and increase the post-processing cost. Many researches have been devoted to the immobilization of photocatalyst particles in various substrates [8-9].

Alginate is a natural polysaccharide from brown seaweed and contains varying proportions of 1,4-linked a–L guluronic acid and b–D–mannuronic acid [10]. It is found that alginate based composites with photocatalysts such as titanium dioxide nanoparticles have high activity for the degradation of organic pollutants with good mechanical properties and compatibility [11]. Therefore, Alginate could be a desirable candidate as a substrate for photocatalytic degradation.

In this study, the bismuth titanate/calcium alginate (CA/BTO) composite beads were prepared by crosslinking the mixture of sodium alginate and $Bi_4Ti_3O_{12}$ particles in aqueous solution. The dye rhodamine B was chose as model organic pollutants to evaluate the photocatalytic activity of the CA/BTO composite beads. The photocatalytic activity of the CA/BTO composite beads prepared with different heat treated bismuth titanate (CA/BTO-700, CA/BTO-800 and CA/BTO-900) was investigated under simulated solar light. The recycling usability of the CA/BTO-700 beads was also tested by photocatalytic degradation of RhB for four times.

2. Experimental

2.1. Materials
Bi_2O_3 and Sodium alginate was purchased from Sinopharm Chemical Reagent Co., Ltd, analytical grade. The TiO_2 was obtained from Germany Degussa Co., Ltd, analytical grade. Calcium chloride ($CaCl_2$) was purchased from Tianjin Dingshengxin Chemical Industry Co., Ltd, analytical grade. The dye Rodamine B (RhB) was analytical reagent grade. Deionized water was used throughout the experiments.

2.2. Preparation of bismuth titanate/calcium alginate bead
The bismuth titanate particles were prepared by molten salt synthesis (MSS) Method [12]. Bi_2O_3 and TiO_2 were mixed with stoichiometric amounts Bi/Ti = 4:3. Meanwhile NaCl and KCl were added as the cosolvents at a mole ratio of NaCl: KCl: $Bi_4Ti_3O_{12}$ = 50: 50: 1. The mixture was grinded for 40 minutes and then heated at 700°C, 800°C and 900°C for 2 hours, respectively. According to the heat treated temperature, the as-prepared products are denoted as BTO-700, BTO-800, BTO-900, respectively.

The bismuth titanate/calcium alginate beads were prepared by a facile method. Initially 0.6 g sodium alginate was added and stirred in the 30 mL distilled water. Then 0.45 g bismuth titanate particles were dispersed into the sodium alginate gel and stirred evenly to form a mixture. Subsequently, the mixture was added dropwise to 1.5% $CaCl_2$ aqueous solution to form the bismuth titanate/calcium alginate beads product. Finally, the obtained beads was immersed in 1.5% $CaCl_2$ aqueous solution for 11 hours and washed by deionized for several times. The prepared bismuth titanate/calcium alginate bead was noted as CA/BTO-700, CA/BTO-800 and CA/BTO-900 according to the added bismuth titanate particles BTO-700, BTO-800 and BTO-900, respectively.

2.3. Degradation of dye Rhodamine B
The photocatalytic activities of the bismuth titanate/calcium alginate beads were evaluated by photocatalytic degradation of organic dye RhB under simulated solar light. A 300 W Xe lamp was used as the light source. Certain amount as-prepared beads containing 0.45g bismuth titanate were dispersed uniformly into 100 mL 5 mg/L RhB solution. The suspensions were magnetically stirred under the simulated solar light. At given time intervals, aliquots of the solution were taken and analyzed on a UV–vis spectrometer (756S, China). The photocatalytic usability was evaluated under light irradiation. After each reaction, the composite beads were collected and washed by deionized water for several times and dried by filter paper.

3. Results and Discussion

3.1. Characterization of the bismuth titanate particles

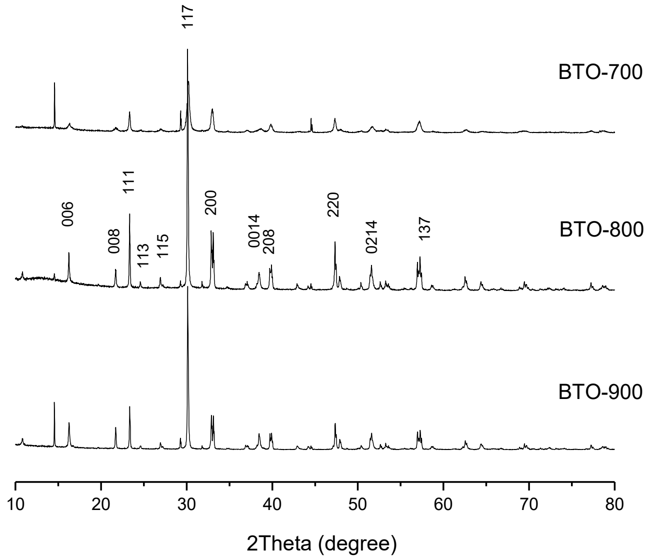

Fig. 1 XRD patterns of the BTO-700, BTO-800 and BTO-900.

Fig. 1 shows the XRD spectra of the as-prepared bismuth titanate particles with different heat treated temperature. XRD patterns of the samples were characterized on a D8 Advance X-Ray diffractometer (Bruker AXS, Germany) with Cu Kα radiation. The XRD patterns shows the crystallinity and phase purity of the as-prepared bismuth titanate particles BTO-700, BTO-800 and BTO-900, respectively. It can be seen from Fig. 1 the as-prepared bismuth titanate particles BTO-700, BTO-800 and BTO-900 was well crystallized. The main diffraction peaks at 16.19°, 21.64°, 23.31°, 30.06°, 32.86°, 39.68°, 47.32°and 57.23° are corresponded to (006), (008), (111), (117), (200), (208), (220), (137) crystal planes of $Bi_4Ti_3O_{12}$ (JCPDS No. 71-1019). The diffraction peaks of bismuth titanate particles with heat treated temperature 700°C, 800°C and 900°C can be well indexed to the pure orthorhombic $Bi_4Ti_3O_{12}$.

3.2. Photocatalytic activity of the bismuth titanate/calcium alginate beads

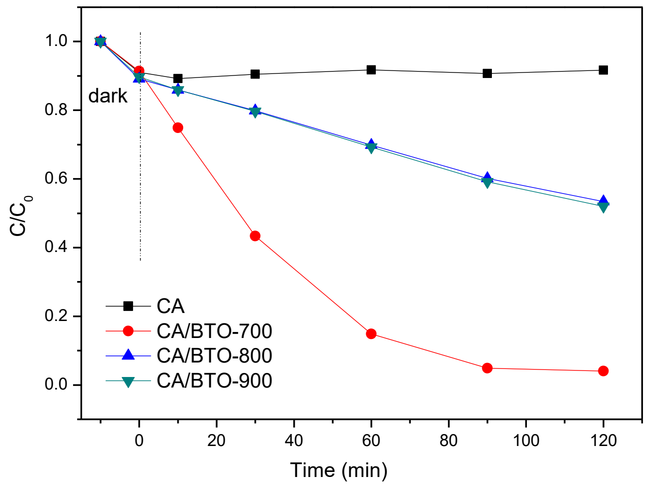

Fig. 2 The degradation profiles of RhB by bismuth titanate/calcium alginate beads CA/BTO-700, CA/BTO-800 and CA/BTO-900 under simulated solar light.

The photocatalytic degradation profiles of dye RhB by the bismuth titanate/calcium alginate beads CA/BTO-700, CA/BTO-800 and CA/BTO-900 were shown in Fig. 2. The calcium alginate beads prepared without bismuth titanate (CA) was used as the control experiment. It can be seen from Fig. 2, the adsorption removal of RhB from aqueous solution by CA is about 10%. The bismuth titanate/calcium alginate beads CA/BTO-700, CA/BTO-800 and CA/BTO-900 also showed certain extent adsorption ability for the removal of RhB and the adsorption removal is nearly 10%, which is close to that of CA. The result indicated that the adsorption for CA had little changed by the addition of bismuth titanate. After 120 min light irradiation, the concentration of RhB in solution changed slightly by the CA, which indicated that the CA has no photocatalytic ability. The removal of RhB is about 96% by the CA/BTO-700, 47% by the CA/BTO-800, and 48% by the CA/BTO-900. The CA/BTO-700 showed the best photocatalytic degradation of RhB compared with CA/BTO-800 and CA/BTO-900.

The Langmuir–Hinshelwood rule was used to describe the photocatalytic degradation process of RhB by the bismuth titanate/calcium alginate beads. The Langmuir–Hinshelwood rule is given as:

$$\ln (C_0/C_t) = kt(\mathrm{min}^{-1})t + a \qquad (1)$$

where k is the apparent reaction rate constant, C_0 is the initial concentration, and C_t is the concentration at the reaction time of t. The Kinetics for the photocatalytic degradation of RhB using bismuth titanate/calcium alginate beads are summarized in Table 1. It can be seen from Table 1, for the kinetics of photocatalytic degradation of RhB, the correlation coefficient were in the range of 0.9863–0.9988. The results indicated that the photocatalytic degradation processes of RhB by the bismuth titanate/calcium alginate beads were fitted well with the Langmuir–Hinshelwood rule. Moreover, the reaction rate constant of the CA/BTO-700 is more than 6 times higher than that of the CA/BTO-800 and CA/BTO-900.

Table 1 Kinetics for the photocatalytic degradation of RhB by bismuth titanate/calcium alginate beads.

The prepared beads	Fitted equation	Reaction rate constant k ($\times 10^2$ min^{-1})	Correlation coefficient, R^2
CA/BTO-700	y =0.02846x	2.846	0.9863
CA/BTO-800	y=0.00435 x	0.435	0.9976
CA/BTO-900	y=0.00452 x	0.452	0.9988

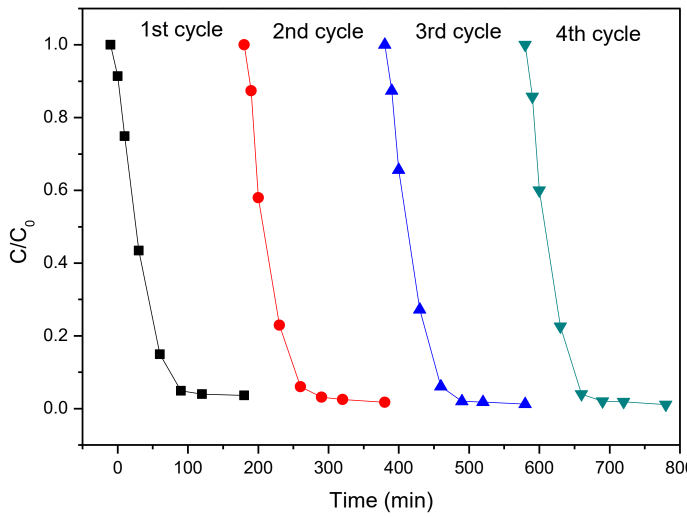

Fig. 3 The reusability of the CA/BTO-700 composite beads for the photocatalytic degradation of RhB.

The reusability of the photocatalyst is the key factor for applying in large scale. Therefore, the photocatalytic reusability of the CA/BTO-700 composite beads was evaluated by the degradation of

RhB for four times. As shown in Fig. 4, the degradation rate of the CA/BTO-700 nearly remains unchanged after 4 cycles in photocatalytic degradation of RhB. The results indicated that there could be no bismuth titanate leached out from the composite beads, and also there was no photocorrosion for the bismuth titanate during the degradation process.

4. Conclusions

In summary, the bismuth titanate/calcium alginate (CA/BTO) composite beads were prepared by cross-linked method. The bismuth titanate $Bi_4Ti_3O_{12}$ particles were immobilized in 1.5% sodium alginate (SA) matrix. The XRD analysis indicated that the as-prepared bismuth titanate particles BTO-700, BTO-800 and BTO-900 was well crystallized and the main diffraction peaks are corresponded to JCPDS No. 71-1019. In comparison with the CA/BTO-800 and CA/BTO-900, the CA/BTO-700 showed the best photocatalytic degradation of RhB. The reaction rate constant of the CA/BTO-700 is more than 6 times higher than the CA/BTO-800 and CA/BTO-900. The photocatalytic reusability of the CA/BTO-700 composite beads was also evaluated. The degradation rate of the CA/BTO-700 was almost unchanged within 4 cycles.

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