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Original Research Paper

TiO_2/void/porous Al_2O_3 shell embedded in polyvinylidene fluoride film for cleaning wastewater

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A B S T R A C T

In order to selectively adsorb hydrolyzed polyacryamide (HPAM) and remove oil from oily wastewater, TiO_2/void/porous Al_2O_3 shell particles (TVAs) were designed and prepared though hydrolysis and calcination; subsequently, the TVAs were embedded into polyvinylidene fluoride (PVDF) to prepare composite films (TVAP films). As polymeric supports, TVAP films were employed to immobilize TiO_2 powder. TVAs were characterized using SEM, TEM, FT-IR, BET while TVAP films were characterized by SEM. The results indicate that the particle size of TVAs is mainly distributed between 700 and 800 nm, core-shell structure has been successfully built. The removal rates of TVAP films prepared under the optimum synthesis conditions for oil and HPAM reach 69.70% and 60.20% respectively, performing attractive properties of mass transfer and adsorption. Therefore, TVAP films are desirable as suitable materials to clean oily wastewater.

1. Introduction

Nowadays with the environment pollution and water resources crisis becoming increasingly serious, wastewater treatment has received growing attention as a promising process for water purification. Wastewater mainly comes from industrial and municipal discharge. Especially, cleaning industrial oily wastewater is very difficult. So far, lots of efforts have been made to clean oily wastewater. Conventional methods such as air flotation, gravity setting, coagulation precipitation and sand filter [1–3] cannot sufficiently satisfy the requirements of wastewater discharge and recycle standard because of their poor continuous operation performance and low oil removal efficiency. Thus it is highly desirable to develop a sustainable and efficient method to clean oily wastewater.

Oily wastewater with many pollutants such as flocculants (HPAM), harming not only the aquatic environment but also human health, is hard to be cleaned. The existence of HPAM leads to the increase of wastewater viscosity and emulsification. In particular, HPAM molecules with unique linear structure can easily wrap with oil droplets of wastewater through the channels of membranes, therefore, membrane technology cannot be employed to efficiently clean oily wastewater containing HPAM [4]. In other to solve the above mentioned problems, much attention has been focused on adsorption method, which is considered as a particularly attractive and effective process for removing contaminants from wastewater. The structure, specific surface area, and selectivity of an adsorbent are the decisive factors for the adsorption process. Generally, the adsorbents with the larger specific surface area and higher selectivity perform the attractive removal efficiency for contaminants. γ-Al_2O_3, as a low-temperature metastable polymorph of transition alumina with abundant surface hydroxyls, has been widely applied in the purification of water owing to its large specific surface area and strong electrostatic adsorption capacity [5–7], especially it is very effective to remove HPAM in wastewater. For instance, Zhang et al. prepared Al_2O_3-coated diatomite materials via the hydrolysis reaction and successfully utilized them to clean wastewater containing HPAM [8]. This is because porous Al_2O_3 materials can attract with HPAM via electro-static interaction (isoelectric point is about 9, showing positive zeta potential values at pH 7), performing selective adsorption capability for HPAM. After treatment by porous alumina, the content of HPAM and suspended solids in the filtrate have been cleaned to

Abbreviations: PVDF, polyvinylidene fluoride; HPAM, hydrolyzed polyacryamide; TVAs, TiO_2/void/porous Al_2O_3 shell particles; TVAP films, TVAs/PVDF composite films.

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meet the recycling standard of wastewater. However, Al_2O_3-coated diatomite cannot degrade or clean other pollutants in wastewater, such as organic macromolecules and microbes. Therefore, researching new materials with multi-functions for cleaning wastewater from industrial discharge has become an important task.

Titanium dioxide (TiO_2) is considered to be a promising photocatalyst for cleaning water due to its excellent chemical stability and photocatalytic activity [9–11], which can effectively degrade organic pollutants (i.e., hydrocarbon and soluble oil) and microbes [12]. However, the separation and recovery of TiO_2 powder from the water after treatment is still a problem that cannot be ignored [13]. In order to address the problem, efforts have been attempted to immobilize TiO_2 nanoparticles on inorganic supports [14,15] or organic carriers [16,17], especially on polymeric supports [18,19]. Compared to inorganic supports, polymeric materials possess high chemical inertness and mechanical stability, which can avoid chemical modification when the TiO_2 particles were embedded into the polymer membranes [20]. But there is a problem that polymeric supports may be photodegraded by the superior photoactivity of TiO_2 nanoparticles. A representative approach to overcome the degradation of polymeric material is fabricating core/shell structure by encapsulating TiO_2 particles into inert inorganic substances [21,22]. In order to recycle TiO_2 particles and further enlarge pore size of the shell, Zhang et al. [23] selectively etched the interior of the silica spheres by a "surface-protected etching" strategy, creating openings on silica shells. The results show that these openings allow the dissolved chemical species to reach the embedded catalytic particles which indeed enhanced mass transfer. Besides, porous Zr-doped SiO_2 shell/TiO_2 core particles with expanded channels (EC-ZSTs) [24] were prepared and embedded into PVDF to prepare EC-ZSTP membranes for photodegrading methyl orange solution and oil in wastewater containing oil. The results indicate the expanded channels of EC-ZSTs can enhance the mass and light transfer, ensuring better photocatalytic performance of EC-ZSTs and EC-ZSTP membranes. Although numerous studies on the preparation of core/shell structure have been reported, how to remove HPAM in the oily wastewater using TiO_2 functional materials is still not investigated. Based on above mentioned investigations and analysis, TiO_2/void/porous Al_2O_3 shell particles (TVAs) built by the synergetic effect of double template agents (CTAB and PEG-400) and hydrolysis of aluminum nitrate in basic solution will show the properties of selectively adsorbing HPAM and removing oil from oily wastewater. In the core/shell structure, the porous Al_2O_3 shell not only effectively protects the polymer carrier from the damage and degradation of the TiO_2 photocatalyst, but also promotes the mass transfer of organic pollutants and ensures a large specific surface area of TVAs. When the TVAs are embedded into PVDF to form TVAP films, the photocatalytic performance and adsorption capacity for HPAM of TVAP films can be expected.

In this paper, in order to selectively adsorb HPAM and remove oil from oily wastewater based on recycling TiO_2 particles, TVAs are fabricated by the synergetic effect of double template agents (CTAB and PEG-400) and hydrolysis of aluminum nitrate in basic solution, and then embedded into PVDF to form films immobilizing TiO_2. The preparation conditions of TVAP films are optimized and the photocatalytic activity of TVAP films is researched and analyzed.

2. Experimental

2.1. Materials and reagents

All chemicals were used as received without further treatment. Tetrabutyl titanate (TBT, AR grade, 98.0%) was purchased from Tianjin Fuchen Chemical Reagents Company. Polyethylene glycol with average MW 400 Da (PEG-400, AR grade, ethylene glycol ≤ 0.18%) was obtained from TianjinBodi Chemical Holding Co., Ltd. Oleic acid ($C_{18}H_{34}O_2$, OA, AR grade), absolute ethanol (CH_3CH_2OH, AR grade, 99.8%), aluminum nitrate (($Al(NO_3)_3{\cdot}9H_2O$, AR grade, 99.0%), cetyltrimethylammonium bromide (CTAB, AR grade, 99.0%), ammonium bicarbonate (NH_4HCO_3, AR grade, $NH_3 \geq$ 21.0%) and acetone (CH_3COCH_3, AR grade, 99.5%) were provided by Tianjin Guangfu Fine Chemicals Co., Ltd. Dimethyl carbonate (DMC, AR grade, 99.0%) was received from Tianjin Chemical Reagent Research Institute. PVDF (1015) was supplied by Solvay Co., Ltd (USA). N,N-dimethylacetamide (DMAC, AR grade, 99.5%) were obtained from Tianjin Damao Chemical Reagent Factory.

2.2. Synthesis of TVAs

The preparation process of TVAs is schematically shown in Fig. 1. Based on our previous work [8], the TVAs were prepared by hydrolysis, calcination, and the detailed procedures are as follows.

Preparation of TiO_2/OA composite particles: The synthesis approach of TiO_2/OA composite particles is similar to literature [24]. First, NaCl aqueous solution was added dropwise into the mixture of absolute ethanol and TBT, and then centrifugated, dried in the oven at 60 °C for 6 h and calcined at 500 °C for 2 h to obtain anatase TiO_2. Second, TiO_2 particles were added into the modifying agent, which consists of oleic acid, absolute ethanol and deionized water (volume ratio 1:2:2), and then centrifuged and dried to obtain the TiO_2/OA composite particles.

Preparation of TVAs: 60 mL of deionized water and a certain amount of CTAB and PEG-400 were mixed and stirred at 40 °C for 30 min. Then 0.2 g of TiO_2/OA composite particles was added to the mixture under magnetic stirring for 30 min. Next, $Al(NO_3)_3{\cdot}9H_2O$ was added to the mixture with 10 min stirring, followed by adding different volume ratios between NH_4HCO_3 solution of 1 mol L^{-1} and $NH_3{\cdot}H_2O$ solution of 0.1 mol L^{-1} to adjust pH value to 9.0. The reaction system was kept under stirring for 10 h, and then aged at 25 °C for 20 h. Afterwards, the as-obtained precursor particles were centrifuged and washed by deionized water, followed by drying at 60 °C for 6 h and calcination at 500 °C for 2 h to obtain TVAs.

2.3. Preparation of TVAP films

The TVAP films were prepared via appropriate phase inversion technology [25]. Firstly, 0.4 g of TVAs was dispersed into the mixture of DMAC and acetone at 55 °C under ultrasonic agitation for 60 min. Next, 2.885 g of PVDF was dissolved into the mixture under ultrasonic agitation for 2 h. Then, 8.4 mL of DMC was added into the mixture under continuously ultrasonic agitation for 30 min to form a transparent sol. Finally, the as-obtained solution was cast onto a smooth and clean glass plate with the desired thickness controlled by a doctor blade. The solvents were evaporated under ambient condition for 10 min. The films were kept in the vacuum drying oven at 90 °C for 2 h.

PVDF films were obtained in the same procedure as described above but without the presence of TVAs.

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