Degradation of oxytetracycline using microporous and mesoporous photocatalyst composites: Uniform design to explore factors

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ABSTRACT

Microporous ZSM-5 and mesoporous MCM-41 loaded with TiO_2 were synthesized to remove oxytetracycline in aqueous solutions. The adsorption of oxytetracycline showed that MCM-41 had higher adsorption capacity than ZSM-5 and that this capacity changed little after TiO_2 loading. Four factors affecting photocatalytic degradation were investigated by uniform design; these factors included the initial pH of oxytetracycline solution, reaction temperature, dosage of catalysts, and TiO_2 content of catalysts. Single-factor experiment confirmed that experimental values agreed with predicted ones by the regression formula of the uniform design. After recycling and reuse for five cycles, the composites retained their degradation performance. Both adsorption and photocatalytic degradation experiments indicated that MCM-41 was more suitable than ZSM-5 for loading TiO_2 to remove oxytetracycline because of the former's better absorption properties. The biomass at the stationary growth phase and the maximum specific growth rate of *Escherichia coli* were used to assess toxicity during photocatalytic degradation, which linearly decreased with increased oxytetracycline degradation efficiency.

1. Introduction

Oxytetracycline (OTC, Fig. 1) is a tetracycline antibiotic, which is widely used in medicine and the livestock and fishery industries. OTC undergoes minimal metabolism and is mainly excreted via urine as prototype into sewage or directly into surface water [1–3]. The broad-spectrum antimicrobial properties of OTC limit traditional biological treatment, so that it can be detected at nanogram to microgram levels in the sewage treatment plant effluent [4,5]. The contamination with antibiotics has introduced antibiotic resistance genes in the environment [6,7].

Many advanced oxidation processes have been developed for removing antibiotics from sewage. Photocatalytic degradation by nanometer TiO_2 is one of the research hotspots [8]. However, nanometer TiO_2 is difficult to recover and reuse. The potentially toxic effects of nanoparticles bring danger to the ecological environment [9,10]. Consequently, the composites with nanometer TiO_2 loaded on various materials were developed [11–14].

Nanometer TiO_2 loading on zeolite possesses strong adsorption ability as well as photocatalytic properties. Pore sizes of different zeolites vary from 10^{-10} to 10^{-8} meter, which closely relates to TiO_2 loading position and adsorption capacity of composites. Therefore, to remove specific contaminants, it is necessary to take pore size of photocatalytic composites into consideration.

The application of experimental design methods in studying photocatalytic process, such as orthogonal experiment [15], central composite design [16–18], and surface response method [19–21], can reduce the amount of experiments and bring out statistically significant results. However, with the methods mentioned above, as the number of factors and levels increase, the number of experiments always exponentially increased. Uniform design were employed to select representative sample sets, thereby reducing the experimental times and the computation. Experimental time is minimized to equal the number of levels. Meanwhile, experimental points were evenly distributed within the test range. More information can be extracted from a relatively small number of experiments by uniform design, which is suitable for multi-level and multi-factor problems [22]. In recent years, uniform design was widely used in many research field, such as engineering mechanical [23–25], analysis chemistry [26,27], material science [28,29] and toxicology [30–32]. However, it is has never been applied to study photocatalytic process, so we try to

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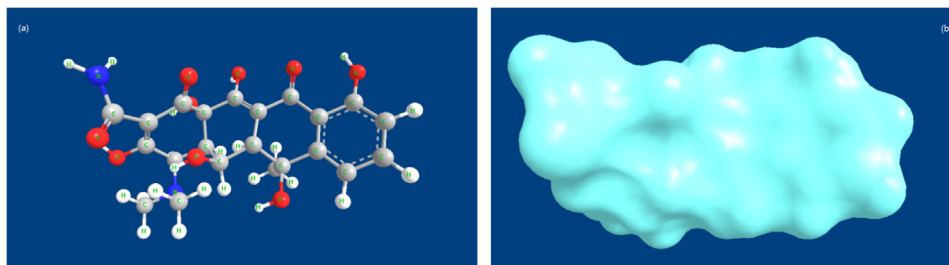
Fig. 1. Stick and ball model (a) and Connolly molecular surface structure (b) of OTC.

prove the usability of the experimental design model in this research field.

In this research, the adsorption and photocatalytic degradation capability of microporous and mesoporous composites, TiO_2 loading on ZSM-5 and MCM-41 zeolite were prepared and compared. The performance of photocatalytic degradation was explored by uniform design with OTC simulated wastewater. Uniform design was adopted to study photocatalytic degradation process for the first time. The predicted results of uniform design and actual results of single factor experiments were compared. To assess the toxic effect of OTC and its subsequent degradation solution to *Escherichia coli*, two calculating methods, the maximum specific growth rate and the biomass at stationary growth phase of inhibition rate were compared.

2. Materials and methods

2.1. Materials

Oxytetracycline hydrochloride (OTC, 95%–100.5%) was purchased from Panreac. The raw ZSM-5 zeolite and TiO_2 (P25) powder, as well as the chromatographically pure acetonitrile and triethylamine were purchased from ACROS. Tetraethyl orthosilicate (TEOS, 98%) and hexadecyltrimethylammonium bromide (CTMABr, 99%) were purchased from Aldrich. Ethanol (99.5%), ethylenediaminetetraacetic acid disodium (EDTA-2Na), ammonium acetate, HCl, H_2SO_4, formic acid, NaOH, and ammonia water (28%) were analytical grade and purchased from SHIYAKU. Ultrapure water with a resistivity more than $18.00 \, M\Omega \, cm$ was prepared by OTUN ultrapure water system.

2.2. Preparation and characterization of the composites

MCM-41 was synthesized according to our previous method [33]. Briefly, 4.6 g of CTMABr was dissolved in 95 mL of distilled water. A homogeneous transparent solution was made by continuously stirring with a laboratory stirrer before ammonia water was added to the solution. The mixture was stirred for 15 min before 8.8 mL of TEOS was added. The mixture was stirred for 12 h at room temperature. The white precipitate was filtered and washed consecutively with distilled water and dried at 100 °C for 8 h. The material was finally calcined at 550 °C for 5 h to burn out the template to obtain MCM-41.

Composites were synthesized by the solid-dispersion method [34]. TiO_2 was uniformly dissolved in ethanol after ultrasonic dispersion for 30 min. ZSM-5 or MCM-41 was added into the suspension with rapid stirring at room temperature for 1 h to enable TiO_2 to be fully adsorbed onto the surface of ZSM-5 or MCM-41. The suspension was dried at 100 °C for 8 h to remove the solvent and calcined at 400 °C for 2 h. The products were finally ground into ultrafine powder and referred to as *x*TZ or *x*TM, where *x* was the weight percent of TiO_2 in the composite.

The crystal phases of the composites were determined with an X-ray diffractometer (XRD, Rigaku Ultima IV). Their shape and fine structure were observed by scanning election microscopy (SEM; Mac Science, MXP18) and transmission electron microscopy (TEM; JEOL, JEM-2000 FX). The element distribution of composites was analyzed by energy dispersive spectroscopy (EDS; HORIBA, EMX) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Agilent, 4100).The specific surface area and pore distribution was studied by an N_2 adsorption/desorption analyzer (Micromeritics, ASAP 2020N).

2.3. Adsorption experiment

The OTC solution of $10 \, mg \, L^{-1}$ was freshly prepared in ultrapure water. The initial pH was unadjusted and ranged from 4.63 to 4.91. The amount of material used was 0.1, 0.2, 0.3, 0.4, and 0.5 g, whereas the solution volume was 100 mL. The materials were mixed in a group of glass conical flasks on a constant bath shaker shielded from light at 125 rpm at 25 °C. Throughout the reaction of 80 min, samples were taken at predetermined time and filtrated using filter membrane (0.2 μm) before analysis.

2.4. Photocatalytic degradation experiment

Photocatalytic experiments were performed in cylindrical reactor with the diameter of 7 cm and height of 40 cm, which were shielded from external light. Ultraviolet (UV) lamp (254 nm, $0.97 \, mW \, cm^{-2}$; APUV-12F, Sparxic) was used as the single light source. The 1 L solution was continuously stirred by a magnetic agitator at 100 rpm. The pH was adjusted with $1 \, mol \, L^{-1}$ HCl or $1 \, mol \, L^{-1}$ NaOH. The temperature was controlled by a constant-temperature water circulator. The initial pH of OTC solution, reaction temperature, dosage of catalysts, and the TiO_2 content in catalysts were changed according to the uniform design. The device is shown schematically in Fig. S1. Throughout the reaction for 60 min, samples were taken at predetermined times and filtered with a filter membrane (0.2 μm) before analysis.

2.5. Recycling experiment

The photocatalyst was recycled and reused 5 times to study its stability. In the first cycle, 0.01 g TiO_2 and the composite with an equal amount of TiO_2 were added to the $10 \, mg \, L^{-1}$ OTC solution without adjusting pH. Subsequently, the 1 L mixture was continuously stirred by a magnetic agitator at 100 rpm. The temperature was controlled at 25 °C by a constant-temperature water circulator. After the reaction for 150 min, samples were purified with a filter membrane (0.2 μm) before analysis. At the end of the first cycle, the photocatalyst was filtered by filter paper, dried at 100 °C, and calcified at 400 °C for 2 h to remove adsorbed intermediates. The same procedure was employed after every cycle of usage.