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Titanium dioxide sol–gel-coated expanded clay granules for use in photocatalytic fluidized-bed reactor

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ABSTRACT

An experimental research into the titania coatings on granulated expanded clay to be used in fluidized-bed photocatalytic reactor was undertaken. The preparation procedures were performed via sol–gel method using dip coating techniques. Two sol–gel compositions based on tetrabutyl orthotitanate and titanium tetraisopropoxide as well as two commercial TiO_2 sols were examined. The impacts of titania precursor concentration, modification of sol–gel by industrially available TiO_2 nanoparticles, the substrate withdrawal speed and thermal treatment conditions on the coatings' properties were studied. The photocatalytic activity of expanded clay-supported titania was evaluated by the degradation of an emerging micropollutant, tetracycline family antibiotic doxycycline. Mechanically stable and active coatings with properties dependent on sol–gel processing parameters were obtained. The application of porous titania sol–gel-coated expanded clays could combine pollutants' adsorption and their photocatalytic degradation. The compromise between coatings' improved photocatalytic performance, on the one hand, and their adhesion and attrition properties, significant for fluidized-bed operation, on the other hand, lead to the determination of appropriate processing parameters.

1. Introduction

The presence of pharmaceuticals in the environment has received a lot of attention in the last decades due to their negative health and environmental effects even at low concentrations [1,2]. Particularly, the occurrence of antibiotics in hospital, residential, dairy and livestock effluents and municipal wastewater with these pollutants passing through the conventional wastewater treatment intact causes their emissions and accumulation in the hydrological environment [3,4]. The pharmaceuticals are regularly monitored at low concentrations (mostly detected at ng L^{-1} levels) all over the world and the introduction of their obligatory monitoring is currently under discussion [5,6].

The public concern on pharmaceuticals in the environment demands the completion of wastewater treatment plants by the technologies for their removal. One of the options for the destructive elimination of such biologically persistent pollutants in wastewater is the use of advanced oxidation processes based on the action of reactive oxygen species. Amongst these technologies, the reactive species formed by photoexcitation of titanium dioxide allow degrading antibiotics [7–9]. Photocatalytic oxidation of tetracycline family antibiotic doxycycline was studied by our group [9] using P25 and sol–gel-synthesized titania slurries with oxidation by-products determined by liquid chromatography combined with mass spectrometry allowing to suggest the reaction pathway. Process favoring pH values, adsorption and photocatalytic reaction rate constants were obtained. Despite obvious ability of photocatalysis to degrade recalcitrant water pollutants, there is a need for the development of reactors and techniques for the catalyst attachment to the bed material.

Different materials were applied as titania photocatalyst support including glass, silica, ceramics, zeolites, stainless steel, activated carbon as well as granular materials like quartz sand, polymers, etc. [10–23]. Fixed-bed reactors have an intrinsic advantage of not requiring the catalyst separation operation, whereas fluidized-bed reactors are considered to reduce mass transfer limitations if compared to fixed bed. These, however, require the lightweight granular material with developed surface area.

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The present study is focused on the preparation of titania coatings on expanded clay granules to be applied in fluidized-bed reactor for the photocatalytic degradation of doxycycline antibiotic.

The lightweight ceramic expanded clays are rarely used as support material, and its utilization for the titania photocatalyst attachment was studied by our group as reported in [9] and by Zendehzaban et al. [24]. In the last study, the adsorption of titania from its propanolic suspensions on expanded clay granules with those floating on the surface of treated ammonia solutions was investigated. However, our previous study showed that the immobilization of titania on expanded clay from its aqueous or propanolic suspensions had not provided the appropriate adhesion of the catalyst onto the support resulting in a catalyst washout during fluidized bed operation. The application of tetraethyl orthosilicate (TEOS)-based sol–gel as a fixator for industrial photocatalyst nanoparticles showed relatively low activity of the coatings if compared to those obtained later with the titania sol–gel.

Due to the attrition and thus the high level of mechanical stress placed on the coated material, the emphasis on the study of adhesion and abrasion resistance properties of the titania coatings should be firstly done. Secondly, the photocatalytic activity of the bed material should be optimized within the acceptable mechanical properties of the coatings.

In this study, the authors tried to overcome the above-discussed issues by the consecutive investigation of several titania precursors based sol–gel compositions to produce coatings on expanded clay with improved photocatalytic and mechanical properties.

2. Experimental

2.1. Preparation of coatings

The titania coatings were prepared on preliminary sieved 2–3 mm fraction of lightweight expanded clay aggregates (Saint-Gobain Leca). Four sol–gel coating solutions based on two different titania precursors, such as tetrabutyl orthotitanate (TBOT, Fluka), titanium tetraisopropoxide (TTIP, Alfa Aesar) and two industrial sols Hombikat XXS 100 (Sachtleben Chemie) [25] and S5-300A (Cristal Chemical Company) [26], were examined.

The mixture of Hombikat XXS 100 and ethanol in a mass ratio of 1:4.1, respectively, was used in the Hombikat XXS 100 based coating procedure (procedure 1); S5-300A sol was applied as coating solution either diluted with ethanol (1:1.4, wt%) or as received (procedure 2).

TBOT-based solution (procedure 3) included addition of ethyl acetoacetate (Fluka) in amount of 1.63–5 g of 2-propanol under continuous stirring. TBOT in appropriate amount of 4.25 and 9.12 g of 2-propanol with preliminary dispersed P25 (Evonik) (9 wt% in 2-propanol) were added slowly to the sol–gel solution.

In TTIP-based coating solution (procedure 4), diethanolamine (DEA, Riedel-de-Haen) of 4.2 g was mixed with 5.6 g of 2-propanol. Then 2.84 g of TTIP and 0.72 g of H_2O were added dropwise under vigorous stirring. Subsequently to 24 h of stirring, 10 g of P25 propanolic suspension were added to the sol–gel solution and final sol was stirred overnight. The sol–gel-coated clay granules without P25 nanoparticles addition to the sol–gel solution were also prepared.

The coatings were prepared by means of dip coating technique. The clay granules were immersed in the sol–gel solution for 10 s and then withdrawn at 1 mm s^{-1} (dip coating machine, Vitando OÜ).

Sol–gel-coated clay granules were treated as follows: the pre-drying stage was performed at 120 °C for 1 or 2 h with temperature increasing rate of 30 °C min^{-1} (procedures 1–3 and 4, respectively). Afterwards, the coatings were dried at 200 °C for 2 h with temperature increasing rate of 30 °C min^{-1} (procedure 1) or calcined at 500 °C for 2 h with temperature increasing rate of 50 °C min^{-1} (procedures 2 and 4) or for 1 h with a rate of 8 °C min^{-1} (procedure 3).

The dipping and drying stages (procedures 3 and 4) were repeated also three times to vary the thickness of sol–gel coatings. Following the third drying step, the samples were heated for 2 h at 500 °C.

The coatings obtained by the procedure 4 were found to be the most stable and effective in doxycycline removal (see Section 3.2). Therefore, the influence of following parameters was studied to further improve the coatings properties: substrate withdrawal speed in the range of 0.5–2.0 mm s^{-1}, calcination temperature 400–600 °C and duration 1–3 h, P25 nanopowder and TTIP precursor concentration of 0–5.5 and 9.9–15.3 wt% in coating solution, respectively.

2.2. Experimental setup of photocatalytic oxidation

Two borosilicate glass tube units with an inner diameter of 30 mm and height of 370 mm with an aperture 146 m^2 m^{-3} were used as reaction vessels. Glass air diffusers were installed at the bottom of each reactor providing the clay granules' fluidization by pressurized air. To take into the account the effect of pollutants' adsorption onto the coated porous clay granules, one reactor was irradiated by the UV-A sources and another was operated in the dark (reference). The UV source consisted of two 15 W low-pressure mercury lamps (Philips Actinic BL) with a maximum emission at 365 nm and UV-B/UV-A ratio of less than 0.2%. Radiation loss was prevented by four flat reflectors positioned around the setup. The average UV-A irradiation intensity was ca. 9 W m^{-2} measured by fiber-optic spectrometer (USB2000 + UV-VIS-ES, Ocean Optics Inc.). The reaction temperature was maintained at 25 ± 2 °C.

Photocatalytic oxidation of 200 mL of doxycycline hyclate (AppliChem) solution with an initial doxycycline concentration of 25 mg L^{-1} was performed with 3.5 g of coated clay granules for 3 h.

The doxycycline concentration was analyzed by the high-performance liquid chromatography combined with diode array detector and mass spectrometer (HPLC-PDA-MS, Shimadzu LC-MS 2020). Phenomenex Gemini-NX 5u C18 110A 150 × 2.0 mm column, inner diameter 1.7 μm, was used with two eluents, 0.1% acetic acid aqueous solution (eluent A), and acetonitrile (eluent B), with total eluents flow of 0.3 mL min^{-1}; starting concentration of eluent B was 5%, increased to 48.5% by 23 min with linear gradient, held at that concentration for 2 min, and then decreased to 9.5% by 30 min, out of 30 min analysis. Mass spectra were acquired in full-scan mode, MS operated in positive ionization mode with interface voltage of 4.5 kV, and detector voltage of 1.1 kV. Diode array detector was set to scan samples at 190–800 nm. The instrument was operated and the results obtained with MS and PDA detectors were handled using Shimadzu LabSolutions software.

Scanning electron microscopy (SEM; Zeiss EVO 50 and EVO MA-15) was performed to visualize the catalyst coating. The structural stability and abrasion resistance of the coatings were characterized by the turbidity of the solutions measured during the fluidized-bed treatment process at 860 nm in Formazin Attenuation Units (FAU turbidity, Hach DR2800). The specific surface area of coated and bare expanded clay granules was measured by Areameter Ströhlein.

To express the results of doxycycline degradation and evaluate the activity of obtained sol–gel-coated clay granules, the photocatalytic oxidation efficiency E, mg W^{-1} h^{-1} [27], defined as the decrease in the amount of the pollutant in mg, divided by the product of UV-A radiation intensity, in W m^{-2}, the surface of the treated solution, in m^2, and irradiation time, in h, was used. The photocatalytically oxidized amount of doxycycline was calculated as the difference between doxycycline quantities removed in photocatalytic and reference experiments. The first number is taking