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Industrial sludge remediation with photonic treatment using Ti–Ag nano-composite thin films: Persistent organic pollutant removal from sludge matrix

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ABSTRACT

Mechanically dewatered industrial sludge (MDIS) was treated using pure and silver-doped thin films (TFs) grown on quartz substrates. TFs were prepared using a sol–gel dip coating technique. The resulting films were annealed at 450 °C for 3 h and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). Mixtures that were homogeneous in the UV A (380 nm) and UV_{vis} (450 nm) regions of the electromagnetic spectrum were used as the irradiation source. The results revealed that illumination with different wavelengths helps to generate well-separated e^-/h^+ pairs, resulting in a decrease in the recombination rate. An electron transfer chain model was also developed using the experimental results. The performance of the applied method was evaluated by observing variations in the sludge bound water content (SBWC), volatile solids removal rate (VSR), and the consumed and generated energy fluxes through endergonic and exergonic reactions. After treatment, SBWC was reduced from 65% ± 1% to 39% ±1 and the highest VSR was measured to be 27 ± 0.1 mg VSS cm^{-2} h^{-1}. The consumed and recovered energy fluxes were 960 ± 151 and 412 ± 26 J g^{-1} $VS_{removed}$, respectively. Raw sludge and polychlorinated biphenyls ($\sum_{15}$PCB) and polyaromatic hydrocarbon ($\sum_{16}$PAH) concentrations were 4356.82 ± 22 μg kg^{-1} and 446.25 ± 4.8 μg kg^{-1}, respectively. The $\sum_{15}$PCB and $\sum_{16}$PAH concentrations in the treated sludge samples were 129.86 ± 22 μg kg^{-1} and 34.85 ± 1.3 μg kg^{-1}, respectively.

1. Introduction

Clean industrial production techniques help decrease the heavy metal content in wastewater and sludge. It has been also reported that Fenton's peroxidation transfers Cd, Cu, and Ni from the filter cake into the filtrate and land application of the residual cake can hence be reconsidered (Dewil et al., 2006; Van de Velden et al., 2008; Appels et al., 2010). However, it is important to mitigate the environmental hazards and risks of emerging organic pollutants in the sludge. Final sludge disposal alternatives including agricultural use, short- or long-term storage, and landfilling have been regulated in several countries due to the presence of persistent organic pollutants (POPs). European Union directive 86-278-EEC regulates the use of residual treatment sludge to prevent harm to the environment (Tunçal et al., 2011a). Studies on fate and removal of persistent organic pollutants (POPs) from industrial sludge are limited. Previous studies also distinguish between adsorption and biochemical oxidation reactions responsible for POP removal from wastewater. Although several studies mention biodegradation as the primary removal mechanism, high POP concentrations in sludge samples that were collected from full-scale plants indicate that adsorption on solid particles is also an important process. In addition, it is well known that some of the organic compounds present in sludge, such as polyaromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), would be resistant to biodegradation (Laturnus et al., 2007; Barret et al., 2010; Van Caneghem et al., 2012). The

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results of a recent study also indicated that carcinogenic and genotoxic responses were still detectable after 124 days of composting (Kapanen et al., 2013).

Efforts to adapt nanotechnology to sludge treatment are very rare. However, the results of this study indicate that integration of TF-based photonic technology to sludge treatment would provide several remarkable benefits including simultaneous sludge dewatering/drying and stabilization (removal of volatile solids (VSR) including POPs and disinfection). The heat generated by lighting and exergonic energy derived through VSR would also provide a reduced energy demand and a sustainable sludge treatment technology. Surface modifications that allow for the use of solar flux to generate photocatalytic VSR could also supply additional energy savings for thermal sludge dewatering/drying.

In this study, mechanically dewatered industrial sludge (MDIS) was treated photo-catalytically using pure and silver-doped thin films (TFs) grown on quartz substrates. TF(s) were prepared using a sol–gel dip coating technique. The resulting films were annealed at 450 °C for 3 h and characterized by XRD, TEM, SEM, AFM, and XPS. Homogeneous mixtures of eight (8W) UV A and (8W) UV_{vis} lamps were combined in a photoreactor. Variations in the sludge bound water content (SBWC), VSR, and the consumed and generated energy fluxes through endergonic and exergonic reactions driven by photolysis and photocatalysis were investigated. The variations in sludge dewatering/drying characteristics were also examined and compared with conventional methods to primarily evaluate the energy requirements. In addition, the fate and removal of polychlorinated biphenyl (PCB)-$\sum_{15}$PCB and polyaromatic hydrocarbon (PAH)-$\sum_{16}$PAH congeners from MDIS matrices were investigated under several experimental conditions. Photocatalytic sludge treatment performances were measured for both pure and Ag_{doped} TiO_2 TF(s) under "UV_{vis}", "UV A" and "UV_{vis} + UV A" irradiation. In all tests H_2O_2 were used as electron acceptor. Effectiveness of TFs were also determined by experiments conducted using uncoated quartz substrates (QS).

2. Material and methods

2.1. Sol-gel preparation

Undoped and Ag-doped TiO_2 TFs were prepared using the sol–gel dip-coating technique. The TiO_2 sol was prepared with titanium (IV) n-butoxide (Fluka) as the precursor, silver nitrate as the source of elemental Ag and ethanol as the solvent. The ethanol was slowly added to titanium (IV) n-butoxide with stirring. A secondary solution was prepared mixing glacial acetic acid with deionized water in order to decrease the kinetics of the hydrolysis and polycondensation. This secondary solution was mixed for one hour and gradually added dropwise to the titanium n-butoxide solution (Legrand-Buscema et al., 2002; Ungureanu et al., 2007). The silver dopant was prepared by dissolving $AgNO_3$ in diluted HNO_3 and ethanol solutions (Lin and Lee, 2010). The optimum Ti: Ag atomic ratio was determined to be 3 (wt%). The molar ratios of titanium (IV) n-butoxide, glacial acetic acid, deionized water and ethanol were 1:6:9:37. After being vigorously stirred for half an hour, a stable and homogenous sol was obtained. The sol–gel temperature was maintained at 35 °C during dip coating to control the film thickness.

2.2. Thin film coating procedures and photoreactor configuration

TF(s) were grown by multiple layer dip-coating on QS. First, the as-prepared wet films were dried at 300 °C for 10 min. Finally, the films were annealed at 450 °C for 3 h. The dimensions of the QS were 50 × 50 × 3 mm in length, width and thickness, respectively. It should be noted that only one side of a carrier (QS) was coated by pure and Ag-doped TiO_2 TF(s) to increase light transmittance. A KSV Nima Medium Dip Coater Unit was used for TF fabrication. The height that the substrate was withdrawn to is 5 mm above the sol–gel, and the speed of the withdrawal and immersion are 60 mm min^{-1}. The immersion time is 20 s, and the stirring speed was 5% less than the maximum speed during the waiting time. The vertical angle between the substrate and the liquid surface was adjusted to 8°. A Luzchem ICH 2 photoreactor was used in the photocatalytic experiments. The photoreactor equipped with eight fluorescent UV A lamps (8 Watt) and eight fluorescent UV_{vis} lamps (8 Watt) provided an illuminated area of approximately 0.092 m^2, which had an active area of approximately 0.061 m^2 that experienced fluctuations of less than 8% in the incident power. The UV A and UV_{vis} power intensities were measured with a power meter supplied by Luzchem. The measured UV A and UV_{vis} energies were 1057 and 1190 J, respectively. The irradiation time and internal temperature in photoreactor were held constant in all of the experiments at 3 h and 25 °C, respectively. Experimental setup used for photocatalytic tests is demonstrated in Fig. 1.

2.3. Structural characterization

The appearance and structure of TF surfaces were studied by SEM that was performed using a JEOL JSM 6060. Prior to SEM analysis, the samples were coated with gold to increase the conductivity. Electron micrographs from the surface were taken utilizing a low voltage (5 kV) charge balance. The surface morphology of the TFs was studied using a Nanosurf Easy Scan AFM. The microscopic structure of the films was characterized by high-resolution transmission electron microscopy (JEOL JEM 2100F HRTEM). The crystallinity, crystallite size and phase relationship of the TiO_2 TF(s) were characterized by XRD analysis. The diffraction data were collected with a Rigaku D/MAX-2200/PC diffractometer utilizing Bragg–Brentano geometry and a Cu-Kα radiation source with a monochromator in front of the X-ray detector. Ultraviolet–visible (UV–vis.) absorbance spectra were obtained using a SHIMADZU UV-1800 instrument. XPS measurements were performed on a Thermo Scientific K-ALPHA operating at 12.0 kV and 3 mA.

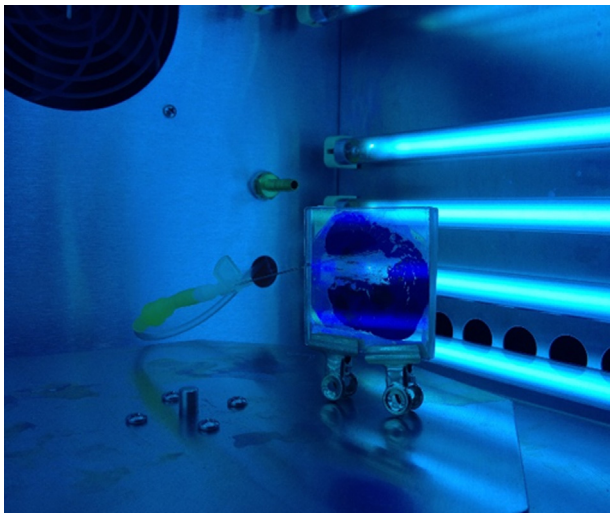

Fig. 1. Experimental setup used for photocatalytic tests.