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Application of immobilized titanium dioxide photocatalysts for the degradation of creatinine and phenol, model organic contaminants found in NASA's spacecrafts wastewater streams

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Abstract

In this project, immobilized titanium dioxide photocatalysis was utilized as a post-treatment technology for the destruction of model organic contaminants found in wastewater streams produced on-board during space exploration. Phenol, a known human carcinogen, and creatinine, a human metabolite found in urine, were the compounds tested in this study. Phenol and creatinine have cyclic structures consisting of six and five member rings, respectively. In addition, creatinine is a methyl guanidine derivative, with almost 40% (w/w) nitrogen. The degradation and carbon mineralization efficiencies of the target contaminants were investigated at different initial concentrations. Their photocatalytic degradation appears to follow *pseudo*-first-order reaction with phenol giving higher organic carbon reduction rates than creatinine. The presence and position of the functional groups of creatinine (amine, imine and peptide bond) are primarily responsible for the significantly slower mineralization. The degradation of creatinine was also tested at different pH_o values. Statistical analysis showed that there is an effect of pH on the treatment of creatinine. Besides the carbon mineralization, the extent of nitrogen mineralization and the mass balance of nitrogen were conducted for three pH values (pH_o 3.0, 6.2 and 11.0). Overall, the transformation of nitrogen was low, and the total maximum conversion (<20%) occurred at basic conditions.

Keywords: Advanced oxidation processes; AOPs; Advanced oxidation technologies; AOTs; Creatinine; Degradation; Films; Immobilized; Nitrogen mineralization; Nitrogen speciation; Phenol; Photocatalytic; Photocatalysis; Titanium dioxide; Wastewater; Water reclamation; Water reuse

1. Introduction

The 3rd of January 2004 went down in history as a step closer to the conquest of the outer space for humanity. It has been more than 3 years after the successful landing on Mars of the two Mars Exploring Rovers (MERs) (Spirit and Opportunity), and since then they have provided data to scientists that support the existence of flowing water on the planet in the past [1]. Such a finding increases the possibility of existence and sustainability of life on the planet and raises hopes of many scientists for the habitation of space by humans. The strong intentions to make human habitation of space a reality are mirrored in National Aeronautics and Space Administration's (NASA) Advance Life Support (ALS) Project [2]. The goal of the project is the creation of a safe and healthy environment in space where human habitation and activities can be supported. Therefore, ALS project includes the study of all the required life support systems that must be cooperated that on-orbit human activities become a reality. Water management, purification and reclamation processes for both multi-crew space missions and habitation are an integral part of this project. Water is stated to be the major component that supports life. The high shipping cost of fresh drinking water to space is a major contributing factor for the high degree of on-going research interest in this field. Thus, the statement ''every drop counts'' has an even bigger meaning for the NASA engineers and crew members. As a result, the quest for new, more efficient, greener, and compact technologies for water purification has always been a necessity. A technology is considered suitable for application in spacecrafts only when it meets specific compliance criteria of NASA. Among them are

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storage and weight limitations of the equipment, maintenance (crew time, cost and special training), operation cost and energy, and shelf life of the equipment [3].

Currently, the International Space Station (ISS) has a water reclamation program based on humidity condensation, hygiene and urine treatment. As a result, wastewater streams formed from urine, urine flush water and personal hygiene water (i.e., shaving, teeth cleaning, bathing, shampoos) having great intrinsic inconsistency require treatment. The treatment of such waste streams poses a challenge mainly because of the complex and fluctuating composition of urine that varies for each individual (sex, nutrition habits, metabolism). To ensure the quality and suitability for use of the product water, NASA has set limitations for its organic and inorganic contents known as spacecraft maximum allowable concentration (SMAC) [4]. For example, the SMAC for phenol is set at 1 $\mu g\,L^{-1}$, while the total organic carbon (TOC) limit is at 500 $\mu g\,L^{-1}$. At present, ISS is testing chemical pre-treatment technologies, such as oxidation with OXONE®, a triple salt of potassium peroxymonosulfate manufactured by DuPont, and physical–chemical technologies including reverse osmosis and vapor compression distillation as potential treatment processes [3].

In this study, immobilized TiO_2 photocatalysis was utilized as a proposed alternative post-treatment technology for NASA's spacecraft wastewater streams. Titanium dioxide photocatalysis is an emerging technology that has the ability to perform very efficiently in water purification. Fujishima et al. have characterized titania as an ''ideal photocatalyst'' [5]. The green characteristics of this technology (no use of hazardous chemicals, no waste production, relatively low toxicity of titanium dioxide compared to some other catalysts, potential for immobilization) combined with the high photocatalytic efficiency and availability of TiO_2, constitute the prime reasons for preferring this technology over others. Titanium dioxide is activated with UV range radiation which is also found in sunlight. Since Mars lacks the protective ozone mantle of Earth, it can allow two to three times more radiation to penetrate. This radiation can be used for activating titania in the planetary habitation water reclamation systems [6].

Unfortunately, application of suspended TiO_2 (slurry) in water purification systems requires post-treatment for removal of the excessive turbidity of the treated samples, especially since there are recent concerns of TiO_2 nanoparticle toxicity [7]. Filtration and precipitation are the most common post-treatment processes for removal of the titania particles. Taking into consideration the fact that the SMAC for turbidity is 1.5 $mg\,L^{-1}$ NTU and the total removal of the nanoparticles from water is difficult and perhaps costly, systems based on slurry titania may not meet the major requirements set forth by NASA. On the contrary, immobilized titanium dioxide may satisfy the major criteria set by the Agency.

In the study described herein, the effects of initial concentration and pH on the degradation of phenol and creatinine with immobilized TiO_2 photocatalysts were investigated.

2. Experimental

2.1. Preparation of photocatalytic films

The TiO_2 films were prepared following a method originally reported by Balasubramanian et al. [8,9], and modified by Chen and Dionysiou [10,11]. The original modification of a plain alkoxide sol with titanium dioxide nanoparticles (Degussa P-25) [9], was further optimized by Chen and Dionysiou in terms of P-25 catalyst loading in the solution (50 $g\,L^{-1}$) and calcination temperature (500 °C). The modified photocatalytic films exhibited increased porosity, photocatalytic activity, and reduced leaching of transition metals (i.e., Cr^{3+}) from the substrate to the surface of the films [10,11]. Thus, we adapted the modification of Chen and Dionysiou for the fabrication of TiO_2 films. Based on the density of anatase TiO_2 (3.89 g cm^{-2}), the film thickness (6.7 μm) and the porosity (35.58%), the amount of catalyst per cm^2 was estimated to be 1.68 mg cm^{-2}. The overall coated area of each stainless steel plate (both sides) was 352.6 cm^2 (21.5 × 8.2 × 2).

2.2. Experimental setup

Fig. 1 shows a schematic of the photocatalytic reactor setup. Four 15 W UV-A lamps (Cole-Parmer), emitting radiation in the range 300–400 nm, with maximum peak at 366 nm and UV-A intensity of 350 $\mu W\,cm^{-2}$ at 6 in. were used for the illumination of the TiO_2 films. The photocatalytic reactor vessel was a clear, fused quartz cell (100 mm × 250 mm × 15 mm). The cell was custom made by Custom Glassblowing of Louisville, Inc. The solution to be treated was aerated continuously with fine air bubbles through a ceramic diffuser placed in the sampling vessel (5). As shown in Fig. 1, the air was passed through an activated carbon column (2) and a humidifier (3), prior to passing into the sampling vessel through the diffuser (4). This prevents any contamination of the solution with volatile organics and the volatilization of water because of the purging. To cool down and avoid the overheating of the

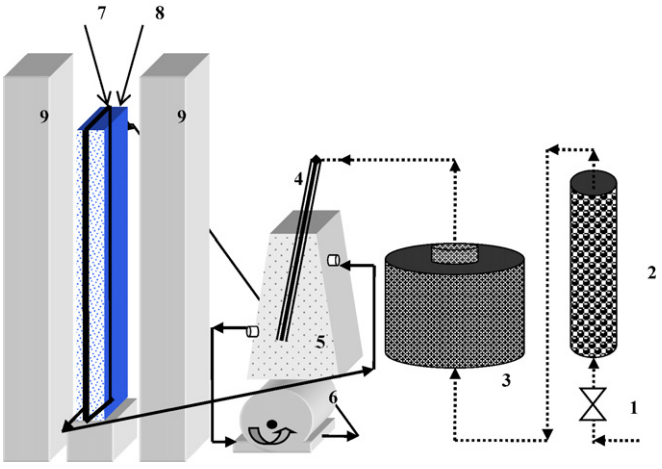

Fig. 1. Photocatalytic reactor setup: (1) air pump, (2) activated carbon column, (3) humidifier, (4) air diffuser, (5) sampling vessel, (6) circulation pump, (7) TiO_2 film, (8) quartz cell, and (9) UV lamps (365 nm).