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ScienceDirect
Catalysis Today 124 (2007) 215–223
CATALYSIS TODAY
www.elsevier.com/locate/cattod

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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Available online 11 May 2007

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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doi:10.1016/j.cattod.2007.03.054

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

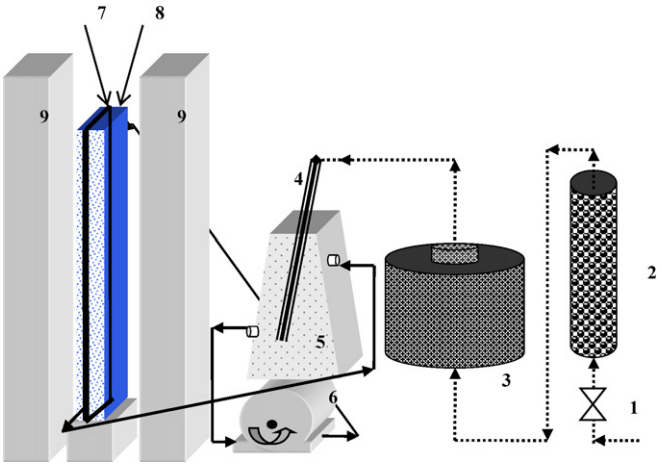


Fig. 1. Photocatalytic reactor setup: (1) air pump, (2) activated carbon column, (3) humidifier, (4) air diffuser, (5) sampling vessel, (6) circulation pump, (7) TiO_2 film, (8) quartz cell, and (9) UV lamps (365 nm).

system, a fan was used. Throughout the experiment, the following conditions were kept constant unless stated otherwise: volume of treated solution (600 mL); air flow (~0.4 L min^{-1}); recirculation rate of the pump (3.85 mL s^{-1}); 1); solution temperature (30–31 °C). The treatment time was 8 h for all the experiments except in the ones dealing with the effect of pH on the degradation of creatinine, which lasted for 25.5 h. All the experiments were performed in triplicates and the corresponding error bars on the graphs illustrate the standard deviation from the mean.

2.3. Analytical methods

Quantification of the target compounds (phenol and creatinine) was conducted using an Agilent 1100 Series High Performance Liquid Chromatography (HPLC) with a Quat-Pump and a UV–vis diode array detector (DAD). For the analysis of samples containing phenol, an Agilent 5-μm diameter Eclipse XD8-C8 (4.6 mm × 150 mm) column was used. The analysis was conducted under isocratic conditions with a mobile phase of 30% acetonitrile and 70% H_2SO_4 (0.01N). The flow rate was set at 1 mL min^{-1} and the injection volume at 20 μL; the column temperature was stabilized at 30 °C and the DAD regulated at λ = 230 nm. For creatinine, a Discovery RP Amide C16 column (5 μm particle, 4.6 mm × 150 mm) purchased from Supelco was used with the same mobile phase as phenol. The DAD was set at λ = 197 nm and the flow rate was set at 0.5 mL min^{-1}; the injection volume was 20 μL and the column temperature was stable at 25 °C. Under these conditions, phenol and creatinine eluted at 4.0 and 3.6 min, respectively. A different analytical method was utilized for the simultaneous analysis of creatinine and creatine (linear amino acid) based on the method of Dash and Sawhney [12]. A Nova-Pak C_{18} Waters 5-μm (3.9 mm × 150 mm) column was used. The HPLC was run in isocratic mode with mobile phase of 100% of 0.045 M of ammonium sulfate $(NH_4)_2SO_4$, at a flow rate of 0.320 mL min^{-1}. The injection volume was set at 20 μL and the column temperature was stabilized at 25 °C. The DAD detector was set at λ = 200 nm for both creatine and creatinine. A Diode Array Spectrophotometer (Model 8452 A, Hewlett Packard) was used to determine the maximum absorbance wavelength of each compound and check the difference in the chromatographs with increasing treatment times and initial pH.

The total organic carbon of the samples was determined in a TOC V CHS Analyzer (Shimadzu). To determine the amount of nitrite/nitrate in the treated samples of creatinine, a Dionex DX 500 Ion Chromatography with a LC 20 Chromatography Enclosure was utilized. The eluent phase was consisted of 3.5 mM of Na_2CO_3 and 1.0 mM of $NaHCO_3$. An IonPac AS14 analytical column (4 mm × 250 mm, Dionex) and an IonPac G14 Guard Column (4 mm × 50 mm, Dionex) were the most suitable for this analysis. The flow rate was 1.2 mL and the injection volume was 10 μL.

For the quantification of the total organic nitrogen concentration of the samples, the Total Kjeldahl Nitrogen (TKN), Nessler Method of HACH (Method #8075) was utilized. The N-NH_3 was initially measured by a colorimetric method of HACH (Salicylate Method #8155). This method has a detection limit at 0.4 mg L^{-1} N-NH_3 and most of the readings were below it. For this reason, an ammonia probe (Accumet), which has higher sensitivity, was utilized instead.

The formation of the creatinine anion was monitored with mass spectrometry (MS). The samples were diluted to ratio 1:1 (sample:solvent) using 100% acetonitrile (electrospray buffer) to maintain the initial solution pH, then directly infused into the electrospray mass spectrometer at a flow rate of 5 μL min^{-1} for data acquisition in the negative ion mode. The instrument used was the Q-Tof 2 mass spectrometer from Micromass UK Ltd. Company. Data acquisition and processing was facilitated by Mass Lynx V4.0 software.

2.4. Statistical analysis

For the statistical analysis of the results, the GraphPad Prism 4 software was utilized. Global fitting was used for the treatment effect in an experiment, i.e., effect of initial solution pH. For the comparison of three mean values (treatment points, initial rates) one-way ANOVA combined with the Bonferroni's multiple comparison test as a post-test were utilized. The null hypothesis tested was that the values are the same (H_o: $\mu_1 = \mu_2$) while the alternative that the values are different (H_a: $\mu_1 \neq \mu_2$). All the tests were two sided for $\alpha = 0.05$.

3. Results and discussion

3.1. Control experiments

To verify that the observed degradation of the examined contaminants is attributed to the photocatalytic activity of titanium dioxide, a series of control experiments with initial concentration of 50 mg L^{-1} for each of the model contaminants at a time were performed. Specifically, the stability of the contaminant solution in the dark, under UV-A radiation and during purging with air and the dark adsorption on the catalyst were conducted. Our results indicate that direct photolysis, dark reaction and volatilization have a negligible effect on the reduction of the concentration of the compounds under study for the tested experimental conditions. The degradation of the compounds occurred only in the presence of both the catalyst and the UV-A radiation.

3.2. Effect of initial concentration

The effects of initial concentration, the degradation, and mineralization of phenol and creatinine for the same initial mass concentration are presented in Fig. 2a and b, for comparison purposes. Fig. 3a and b shows the degradation of creatinine at a wider range of initial concentrations. In all these figures, the degradation curves of phenol (Fig. 2a) and creatinine (Figs. 2a, 3a and 4a) follow exponential decay and the data were fitted as *pseudo-first-order* kinetic model. The obtained values of the kinetic constants (min^{-1}) were transformed to (h^{-1}) and then divided with the surface area

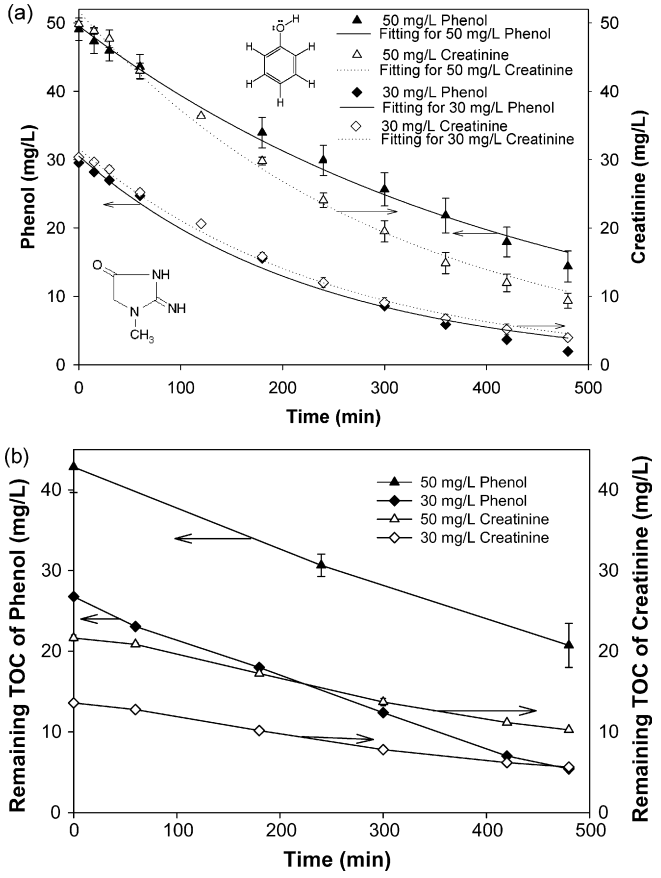


Fig. 2. Degradation (a) and remaining TOC (b) of 30 and 50 mg L^{-1} of phenol and creatinine.

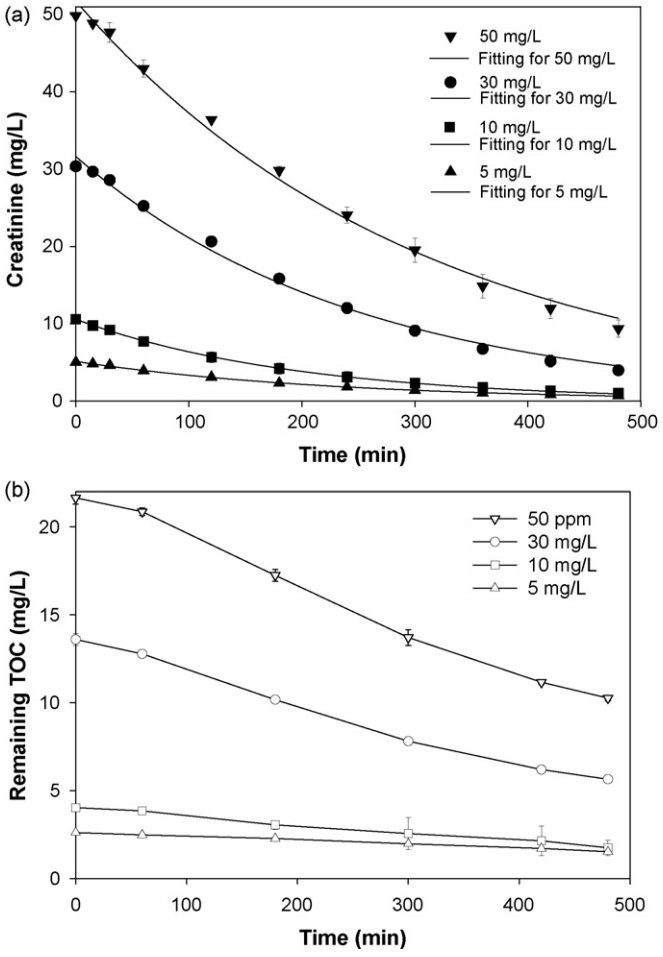


Fig. 3. Remaining creatinine (a) and TOC (b) at different initial concentrations (5, 10, 30 and 50 mg L^{-1}).

of the photocatalytic films (352.6 cm^2) for consistency with previous studies with 4-chlorobenzoic acid [8–11]. The kinetic constant (h^{-1} cm^{-2}), the adjusted R^2 of the curve fitting, and the average initial rates of degradation (averaged over 120 min) are presented in Table 1.

The obtained kinetic constants for phenol and creatinine were in the same range as the one obtained for 4-chlorobenzoic acid with the same photocatalytic films [11]. The initial rates of degradation increase with increasing initial concentration of the contaminants for phenol and creatinine, with the effect being more pronounced for creatinine than for phenol. Fig. 2b shows the reduction of the organic carbon for the same experiments. For the two initial contaminant concentrations (30 and 50 mg L^{-1}) phenol had higher percentage of carbon removals than creatinine: 80% versus 59% and 80% versus 52%, respectively. Since phenol has almost double organic content than creatinine (76.5% versus 42.2%), the results suggest that the formed intermediates of phenol are more susceptible to undergo further degradation than those formed from creatinine. Moreover, the TOC removals of the target compounds (Fig. 2b) were fitted as zero-order kinetics, because the reduction of TOC proceeds slower (multi-step process) than the removal of the primary compounds. In the zero-order kinetic model, the rate of degradation of a compound is constant and independent of the concentration ($dC/dt = a$). The slopes for 50 and 30 mg L^{-1} of phenol are very similar, -0.046 ± 0.003 and $-0.045 \pm$

Table 1
Average initial degradation rates

Contaminant	Phenol		Creatinine						
Conc. (mg L^{-1})	30	50	5	10	20	30	50	20	20
Conc. (mM)	0.319	0.531	0.044	0.094	0.175	0.268	0.440	0.175	0.175
pH_o	6 ± 0.3	6 ± 0.3	6.2 ± 0.1	6.2 ± 0.1	6.2 ± 0.1	6.2 ± 0.2	6.2 ±0.2	3.0 ± 0.1	11.0 ± 0.1
Initial rate (mM min^{-1}) × 10^4	9.10	9.36 ± 0.26[a]	1.43 ± 0.17	3.63 ± 0.34	7.71 ± 0.67	7.16 ± 0.32	9.90 ± 0.26	5.23 ± 0.94	7.42 ± 0.30
k (h^{-1} cm^{-2})×10^4	7.285	3.914	7.351	8.627	11.170	6.878	5.585	10.040	9.529
Adjusted R^2	0.987	0.993	0.999	0.999	0.998	0.995	0.994	0.981	0.999

[a] Standard deviation from the mean.

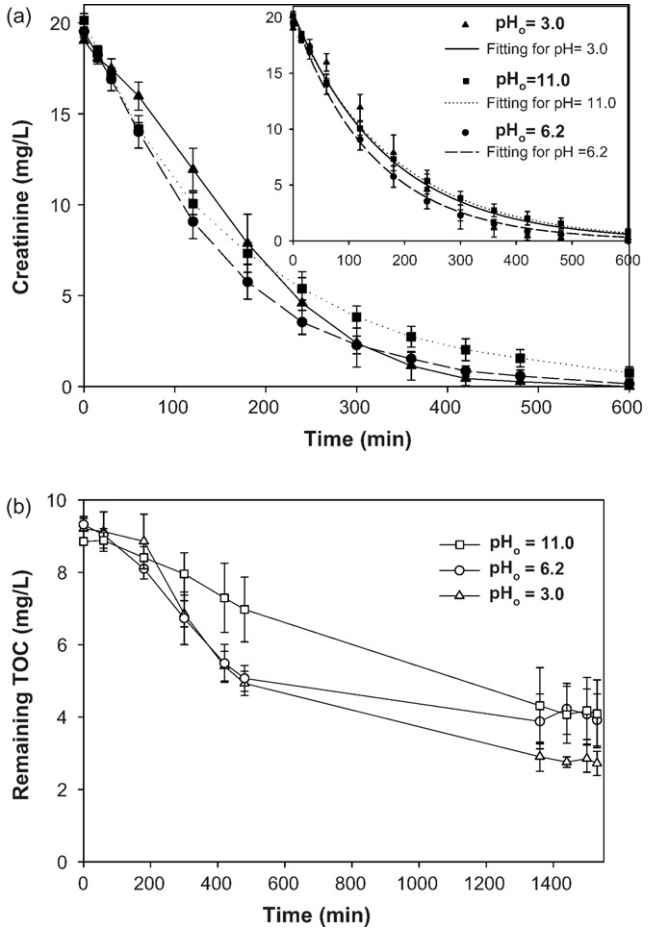


Fig. 4. Remaining creatinine (a) and TOC (b) at different initial pH values (3.0, 6.2 and 11.0).

0.001 mg L^{-1} min^{-1}, respectively, and comply with the zero-order model. The same values for creatinine are -0.025 ± 0.001 and -0.017 ± 0.001 mg L^{-1} min^{-1}, respectively. To explain these findings we refer to the work of Horikoshi et al. [13]. In this study, α-amino acids that differ in the R group (–CH_3, –CH_2OH, –$CH_2C_6H_5$) were degraded with TiO_2 P-25 nanoparticles in suspensions. Phenylalanine (R = –$CH_2C_6H_5$) gave the lowest mineralization (59%) and the authors stated that only the phenyl-carbons were mineralized, while the carbons in the aliphatic chain did not. This finding supports our results of the higher mineralization of phenol to creatinine. It also supports that the presence and the position of heteroatoms in different functional groups in creatinine's chemical structure such as amine and imine, influence both the degradation rate of the primary compound and the mineralization of carbon [13,14].

3.3. Effect of initial solution pH

The kinetic constants for the pH values studied were estimated by fitting the degradation curves considering a first-order reaction. To verify the effect of initial pH solution on the degradation of creatinine the experimental results where statistically analyzed using global fitting. The null hypothesis tested was for the k values to be similar for the three pH values. The test gave a probability of 0.0049 for the k to be the same, therefore the kinetic constants differ statistically and there is indeed an effect of pH on the degradation of creatinine.

For these experiments, the pH of the treated solution was monitored throughout the treatment. At acidic conditions, the pH was adjusted to 3.0 with hydrochloric acid (HCl 36%) and remained stable, with a negligible increase from 3.04 to 3.09, after 25.5 h of treatment. Changes in the pH during treatment were observed for initial pH_o 6.2 and 11.0, with the first one showing a slight increase from 6.2 to 7.2. For initial pH_o 11.0 (adjusted with 0.5 M of NaOH) there was a steady drop in the solution pH of one unit within 4 h of treatment, followed by a drop of two more units in the next 3 h to be stabilized at around pH_f 8.0 for the rest of the treatment.

The initial rate (IR) of degradation of creatinine was also estimated for the three pH values (Table 1). For neutral and basic pH, the rates were very similar while for acidic conditions the initial rate of degradation of creatinine decreased considerably (∼32%). The values of the IRs for each solution pH were statistically analyzed with one-way ANOVA combined with the Benferroni's multiple comparison method and the results (summarized in Table 2) support our previous statements.

At neutral pH, the complete removal of 20 mg L^{-1} of creatinine was achieved after 8 h of treatment and the corresponding carbon mineralization was $46 \pm 4\%$. The treatment was prolonged to 25.5 h to test whether mineralization can be completed as well. The final TOC removal was $58.0 \pm 8\%$, resulting in only 12.0% increase of TOC removal in 17.5 h. In acidic and basic pH the removal of creatinine was completed, respectively, within 8 and 10 h of treatment, and the TOC removals at $t = 8$ h were, respectively, $54 \pm 5\%$ and $21 \pm 10\%$. It is noteworthy that the TOC removal reached plateau at the 23 h of treatment (Fig. 4b). Possibly the remaining carbon is directly bonded to nitrogen and therefore the completion of the mineralization is extended [13,14]. Same as before, the TOC values were analyzed with the appropriate statistical methods to confirm their differences and similarities (results not shown here).

Based on the experimental results and the statistical analysis, a direct correlation is observed between the TiO_2 photocatalytic efficiency for purification and mineralization of the model contaminants and the solution pH. The number of available adsorption sites on the catalyst is susceptible to change with pH

Table 2
One-way ANOVA and Bonferroni's test for the initial rates (IR) at the three pH values

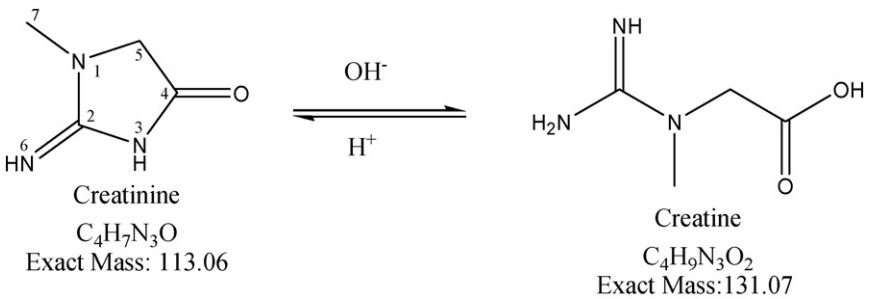
One-way ANOVA	No. of groups	P value	F value
IR pH 3, pH 6 and pH 11	3	0.0093	18.74
Comparison tests	**Mean diff.**	t	P value
IR pH 3 vs. IR pH 6	−0.0002478	5.594	<0.05
IR pH 3 vs. IR pH 11	−0.0002194	4.952	<0.05
IR pH 6 vs. IR pH 11	0.00002842	0.6417	>0.05

variations of the solution. Moreover, pH changes can also alter the overall charge of the primary and secondary contaminants and the catalyst, and consequently the adsorption rate/mechanism on the active sites of the catalyst. In addition, pH affects the oxidation potential of hydroxyl radicals and the Fermi level of the semiconductor [15,16]. As the pH increases, the overall surface charge of TiO_2 changes from positive ($pK_{a1} = 2.6$) to neutral to negative ($pK_{a2} = 9.0$) with the point of zero charge being at pH ≈ 6.4 [17]. Phenol has a $pK_a = 9.89$ and at the treated pH (pH 6.0) both the catalyst and phenol are neutral [18].

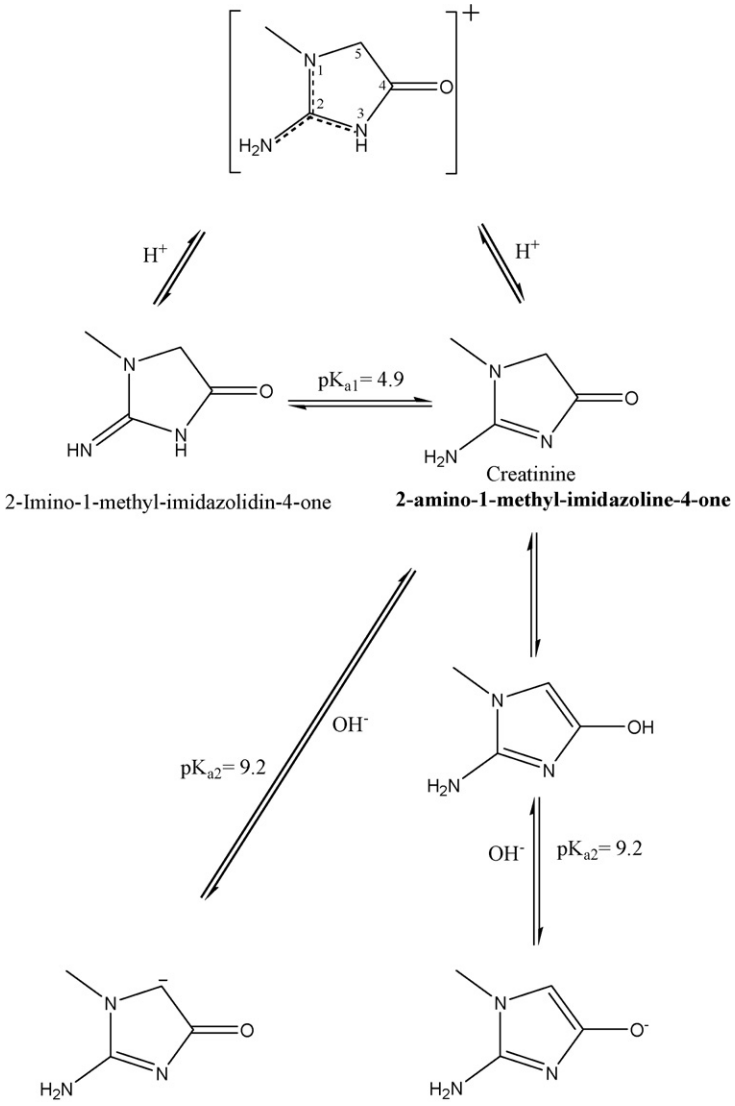
Creatinine has a more complex structure than phenol and to explain the changes in the charge that creatinine undergoes in correlation with pH, it is necessary to examine its structure. Creatinine is classified as an amino acid but does not follow the structural rules of the 20 ''standard'' basic α-amino acids that are used for protein biosynthesis. In the α-amino acids, the amino and carboxylate functional group are attached to the same carbon. On the contrary, creatinine is the cyclic moiety of creatine, where the amine and the carboxyl ends react with each other to form a peptide bond (Schematic 1). Both creatine and creatinine are very weak bases and in aqueous solutions are not considerably dissociated. Creatine is readily converted to creatinine under acidic conditions [19], while creatinine is hydrolyzed to creatine under basic conditions [20,21]. In this study, we observed partial hydrolysis of creatinine only at strong basic conditions (pH 12.5). We chose pH_o 11.0 to study the degradation of creatinine at basic conditions because of the solution stability (in terms of creatinine concentration and pH) and the absence of creatine formation after 4 h of stirring in the dark.

Alouini and Seux [21] reported that during the titration of creatinine with a strong acid, it was indicative that only one protonation occurs, either in the nitrogen in the cyclic structure or in the imine group. Following studies proved that the protonation is found in the N-3 [22]. Therefore, at pH ≤ 3.0, creatinine adapts a unique cationic structure (creatinium cation) as shown in Schematic 2. At pH values close to its $pK_{a1} = 4.84$ [23] creatinine, now neutral, alters structures between two tautomers, with the 2-amino-1-methyl-imidazoline-4-one being the most stable in aqueous solutions [22,24]. At basic conditions, the structure and the charge of creatinine is not clear from the cited literature studies [25–30]. Wollenberger [25] utilized UV-spectroscopy to study the absorption of creatinine at different pH values. He reported that for pH values between 6.5 and 12.3 creatinine has neutral charge. This opposes considering the pK_{a2} of creatinine, which is set at 9.2 [18]. Vasiliades and Butler conducted independent studies that dealt with the reaction and identification of the formed complex between creatinine and picric acid under alkali conditions (pH ≥ 13.0) [26–30]. In this study, we were interested to know the charge of creatinine at dilute basic solutions, such as pH 11.0, in order to explain the degradation behavior of creatinine under our experimental conditions. For this reason, we utilized mass spectrometry in negative ion mode and measured the appearance of creatinine anion at pH values from 6.2 to 12.5. Acetonitrile was chosen as the electrospray buffer to eliminate any changes of the initial pH. The concentration of creatinine was kept stable at 20 mg L^{-1}, for all the pH values. At neutral pH, the appearance of the creatinine anion (*m/z* 112.1062) was negligible. With increasing pH there was a steady increase of the anion counts with a maximum at pH 11.14, follow by a drastic drop at pH 12.5, possibly because of the formation of neutral creatine ($pK_{a2} = 14.3$ [18]). Our MS results prove that creatinine has an inherent negative charge at pH 11 (Fig. 5). As far as where the charge is located, this is not clear from the above-mentioned studies of creatinine with picric acid. Vasiliades [26] stated that under his experimental conditions, the formation of the picric–creatinine complex proceeds from the oxygen (O^-) of the enolic bond of creatinine while Butler [28,29] stated that creatinine forms a carbanion and the reaction proceeds from the carbon (C^-) (Schematic 2).

Based on all of the above, the surface charge of the catalyst and creatinine is expected to be positive, neutral and negative for pH_o 3.0, 6.2 and 11.0, respectively. At acidic pH, both catalyst and primary contaminant (creatinine) are positively charged, hence the adsorption on the surface of the titania is limited. In addition, chloride ions have negative effect on the degradation and are considered as inhibiting anions [15]. The combination of inhibiting anions and acidic pH has a negative effect on the efficiency because of the competition with the target compounds for adsorption on the oxidizing sites of the catalyst and the increased formation of anionic radicals. The latter have limited oxidation properties compared to the hydroxyl radicals, so their presence might contribute to the initial lag in the degradation of creatinine [16]. Regardless, the initial delay in the degradation of creatinine at acidic pH opposes the increase in the total organic carbon removal at $t = 8$ h compared to the other pH values (Fig. 4a and b). At neutral pH, no repulsive forces between the catalyst and the primary contaminant are developed, throughout



Schematic 1. Structures of creatine and creatinine, and chemical properties.



Schematic 2. Changes in charge of creatinine with pH and possible structures.

the degradation. For basic pH, initially the creatinine and the catalyst were negatively charged. During the photocatalytic degradation of organic contaminants, small molecular weight, weak organic acids can form [31,32]. Preliminary studies with MS in negative mode support the formation of such organic acids during the photodegradation of creatinine. Specifically, traces of oxalic, acetic and glyoxylic acid were detected. Because of the initial basic pH, these acids dissociate to their corresponding anions (repulsive forces) resulting in the observed pH drop. The delay in the mineralization of creatinine at basic pH at $t = 8$ h compare to the other two pH values, and the continuous pH drop can be explained by the presence of these acids (Fig. 4b).

3.4. Nitrogen speciation during the degradation of creatinine at acidic, neutral, and basic pH

The presence of the three nitrogens in the structure of creatinine contributes to the lower carbon mineralization of creatinine compared to phenol. Identification of the speciation of nitrogen before and after the treatment of 20 mg L^{-1} of creatinine with TiO_2 photocatalysis is believed to provide a better understanding of our findings. The samples were monitored for TKN, NH_4^+, NO_2^- and NO_3^-.

Previous studies with the TiO_2 photocatalysis of "standard" amino acids such as L-alanine, L-serine and L-phenylalanine, reported high carbon mineralization yields (90, 98, 59%) and high nitrogen conversion yields (97, 87, and 91%, respectively) [13]. It is well established that the degradation of α-amino acids with free radicals proceeds through an initial step of deamination and the intermediate production of α-keto acids [33], resulting in high nitrogen conversion yields. In this case, the formation of nitrogen species was limited and slow (therefore only the initial and final samples were analyzed) (Table 3) because creatinine follows a different mechanistic pathway and its overall organic nitrogen content remains stable. Only for the basic pH a substantial decrease of <20% in the

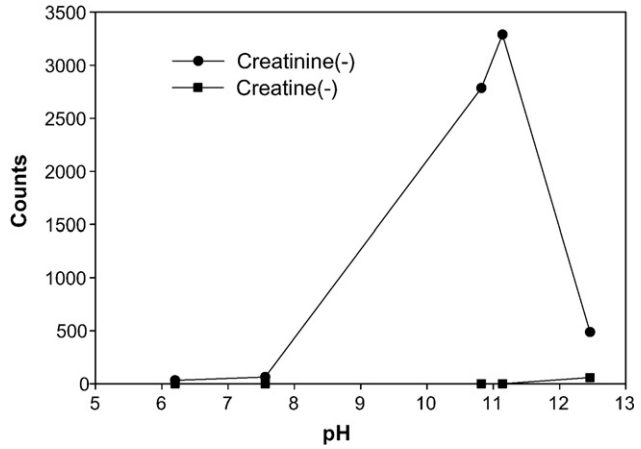


Fig. 5. Appearance of the inherent negative charge of creatinine and creatine with the solution pH.

Table 3
Nitrogen mass balance for acid, neutral and basic initial pH

Sample	TKN (mg L^{-1})	N-NH_4^+ (mg L^{-1})	N-NO_2^- (mg L^{-1})	N-NO_3^- (mg L^{-1})	Total (mg L^{-1})
Initial pH_o 3.0	7.875	0.120	0.000	0.000	7.995
Final pH_o 3.0	7.500	0.163	0.000	0.074	7.737
Initial pH_o 6.2	7.875	0.075	0.000	0.000	7.950
Final pH_o 6.2	7.500	0.530	0.000	0.254	8.284
Initial pH_o 11.0	7.875	0.063	0.000	0.000	7.938
Final pH_o 11.0	6.375	0.400	0.000	1.178	7.953

organically bonded nitrogen was observed. Calza et al. [32], reported that guanidine (a compound with similar functional groups as creatinine) after 70 h of treatment with TiO_2 in slurry, gave a ratio of $[NH_4^+]/[NO_2^-] = 1/3$. We have observed a similar ratio but only for the solution at basic conditions. Overall, the increase of nitrogen transformation follows the order of: pH_o 3.0 < pH_o 6.2 < pH_o 11.0. Preliminary results on the reaction-by-products at different initial pH values suggest that most of the intermediates have at least one nitrogen in their structure. A more complete discussion on the intermediates will be given in a follow-up publication.

4. Conclusions

In this study, we investigated the degradation of phenol and creatinine by immobilized TiO_2 photocatalytic films. We focused on the effect of initial contaminant concentration (phenol and creatinine) and the effect of initial pH of the treated solution for creatinine. The effect of initial contaminant concentration was conducted in super-quality water without the adjustment of pH with buffer solutions. The initial rate of degradation (mM min^{-1}) for creatinine increased with increasing initial contaminant concentration. For phenol the rates for 30 and 50 mg L^{-1} were almost identical possibly because of the higher competition between the parent and the forming intermediates for reaction with the active species (hydroxyl radicals). In general, the carbon mineralization efficiencies for phenol were higher than those of creatinine. We used statistical tests to prove that there is an effect of pH on the degradation of creatinine. An initial delay on the degradation of creatinine was observed only in acidic pH, while for neutral and basic pH the rates were similar. This delay can be attributed to the surface charge of the contaminant and the catalyst. The removal of creatinine was completed between $t = 8$ and 10 h for the three pH values. The carbon mineralization at the same time interval was significantly lower for basic pH compare to acidic and neutral. When the treatment was prolonged to $t = 25.5$ h the mineralization percentage did not differ statistically for the three pH values. We have established through mass spectrometry that creatinine is negatively charged at pH 11. Because of the high nitrogen content of creatinine the concentration of TKN, NH_4^+, NO_2^- and NO_3^- was measured as well. The conversion of nitrogen increases from acidic pH to neutral, with the basic pH giving the maximum conversion. A ratio of $[NH_4^+]/[NO_2^-] = 1/3$ was observed for basic pH only. The limited nitrogen transformation is mainly attributed to the unique cyclic structure of creatinine.

Acknowledgments

This research was funded in whole by a grant from the Office of Biological and Physical Research of the National Aeronautics and Space Administration (NASA) (NRA grant number NAG 9-01475). Dr. Dionysiou is grateful to the National Science Foundation for partially funding this project through the NSF-Career Award (BES-0448117). We are thankful to Dr. Stephen Macha, Director of Mass Spectrometry Services of the University of Cincinnati for his assistant with the TOF-MS and to Mrs. Usha Nambiar for her assistance with the experiments.

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