Self-rotating photocatalytic system for aqueous Cr(VI) reduction on TiO₂ nanotube/Ti mesh substrate

Youngji Kim, Hyunku Joo, Namguk Her, Yeomin Yoon, Chang-Ha Lee, Jaekyung Yoon

Abstract

In this study, a self-rotating photocatalytic system is applied to reduce toxic Cr(VI) to non-toxic Cr(III) in aqueous solution under UV irradiation. To overcome the limitation of powdery photocatalysis, a novel approach towards a photocatalytic system for aqueous Cr(VI) reduction including self-rotating TiO₂ nanotubes on a Ti substrate (mesh type) was established.

For the preparation of TiO₂ nanotubes on the Ti substrate, Ti mesh (10 cm × 10 cm) was anodized at 50 V to 25 °C for 25 min with mixed electrolytes (NH₄F–H₂O–C₂H₆O₂), and then annealed at 450 °C for 2 h in ambient oxygen at a flow rate of 400 mL min⁻¹. The fabricated TiO₂ nanotube arrays were uniformly grown on Ti mesh and surface characterizations was performed through the measurements of SEM, XRD, and zeta potential.

The HRT (Hydraulic retention time) and rotating speeds were significantly affected by inlet flowrate in this reactor being decreased and increased, respectively, with increasing inlet flowrate. Hence, the efficiency of photocatalytic Cr(VI) reduction was observed to be highest up to 95% at the 90 rpm. In addition, the rate of Cr(VI) reduction was increased by increasing the number of TiO₂/Ti meshes.

1. Introduction

Photocatalysis has been recognized as an attractive technology for water splitting hydrogen production and associated environmental purification processes. During the past several decades, numerous studies have been developed to synthesis TiO₂ catalysts...
of different scales, characterize their physical properties, and determine the performance of their surface oriented photocatalysis. However, the photocatalytic process has been simultaneously criticized as being uneconomical compared to the other systems, due to their inherently low efficiency, and the limitations of immobilization [1].

Conventional photocatalyst has related to fine particles being applied in the form of slurry. This is associated with the amount of surface active sites in TiO₂ suspensions. On the contrary, the immobilization of photocatalysts into the substrate (e.g. Ti metal) decreases the amount of active sites and mass transfer limitations, which results in operational limitations. Although the different types of TiO₂ catalyst slurries show a considerable preference in terms of their physical and chemical properties, the main problem of catalyst recovery after reaction remains [2,3]. For this reason, advanced strategies are needed to avoid the loss of catalyst through processes such as post-separation and fixation.

One strategy is catalyst recovery, which can be achieved through hybridization processes such as sedimentation [4] or various membrane filtrations [5-7]. Another strategy is fixation of the catalyst to immobilize the self-grown nanotubular TiO₂ photocatalysts on various kinds of metal substrates [8-11]. The band-gap energy of TiO₂ is 3.2 eV, which is equivalent to UV light with a wavelength of 380 nm, and TiO₂ is therefore photoexcited by near UV illumination. The holes that are generated on TiO₂ are highly oxidizing, and there is an abundance of literature relating to the utilization of TiO₂ in the oxidative degradation of organic contaminants by OH radicals (OH•). In addition, inorganic species with reduction potentials more positive than that of the conduction band of a semiconductor, can consume the electrons and complete the redox reaction cycle. Recently, increasing attention has been paid to the photocatalytic reduction of inorganic contaminants. The TiO₂ photocatalytic reduction process has been reported to be effective for the removal of various toxic metal ions, such as mercury [12], arsenic [13,14] and chromium [15-19].

Especially, hexavalent chromium (Cr(VI)), used as target pollutant in this research, is toxic to most organisms, carcinogenic to animals, and causes irritation and corrosion of the skin in humans. It is highly soluble in water and forms the mono- and divalent oxyanions, chromate [CrO₄²⁻] and dichromate [Cr₂O₇²⁻], respectively, depending on its concentration and pH. Hexavalent chromium compounds are more toxic than trivalent chromium (Cr(III)) due to their high water solubility and mobility [20,21]. On the other hand, Cr(III) is readily precipitated or sorbed on a variety of inorganic and organic substrates at neutral or alkaline pH. Cr(VI) has a toxicity which is one hundred times higher that of Cr(III) and therefore, the reduction of Cr(VI) to Cr(III) is highly desirable in order to decrease the toxicity and contain the mobility of chromium ions [22,23].

In our previous studies, we fabricated various TiO₂ nanotubes on titanium substrates with anodization technology for the purposes of photoelectrodes for hydrogen production [24-27], as well as photocatalyst for water treatments [28,29].

Hence, we focus on the improvement of reaction performance of TiO₂ nanotubes on Ti meshes which are installed on rotating-axis impellers and automatically revolved by hydraulic momentum. In addition, we investigate the photocatalytic hexavalent chromium (Cr(VI)) reduction with the self-rotating TiO₂ for this study.

2. Materials and methods

2.1. Materials

Commercially available titanium mesh (1.2 mm thickness, Hyundai Titanium, Korea) was used for this experiment. Ethylene glycol (C₂H₅O₂, 99.8%), Ammonium fluoride (NH₄F, ≥99.99%), 1.5-Diphenylcarbazide (C₁₃H₁₄N₅O₅, A.C.S. reagent) were purchased from Sigma–Aldrich Chemical Co. and did not require any further purification. Hydrofluoric acid (HF, Duksan, Korea) and Potassium dichromate (K₂Cr₂O₇, Oriental chemical industry, Korea) were of extra pure grade.

2.2. Preparation of TiO₂ nanotubes on Ti mesh

Titanium mesh was cut into pieces (100 cm², 10 cm × 10 cm) prior to anodization. Potentiostatic anodization was performed in a two electrochemical cell which was connected to a DC power supply and programmed by computer (CIMON-SCADA, KDT systems, Korea). An iron foil was used as a counter-electrode (10 cm × 10 cm, 0.25 mm thickness, 99.5% purity, Goodfellow, England), with magnetic agitation in a mixture of chemical electrolyte consisting of NH₄F–H₂O–C₂H₅OH. The nanotubular TiO₂/Ti was then annealed in an ambient oxygen. The detailed compositions of the anodization solution and fabricating conditions are summarized in Table 1. The fabricated samples, which was cut into 10 pieces (each size of 10 cm², 2 cm × 5 cm), were fixed on a rotating axis in reactor.

2.3. Experimental set-up and analysis

A schematic diagram of the total reaction system is shown in Fig. 1a. The reaction system is composed of the three major components: tubular reactor vessel, self-rotating body including TiO₂ nanotubes on Ti meshes, and UV light source. This system also included a flow-meter, pump, tachometer, and reservoir associated with the chiller to maintain reaction temperature constant and chemical addition to control pH.

As illustrated in Fig. 1b, the tubular shape reactor vessel was made of quartz, with an inner diameter of 7 cm, a thickness of 3 mm, a length of 12 cm, and a volumetric capacity of 325 mL (total volume of 1000 mL). The self-rotating body containing impellers, and its vertical axis was made of Teflon, and fabricated TiO₂ nanotubes on titanium meshes (maximum 8 meshes) could be easily attached/detached to the vertical hollows on the axis of the self-rotating body submerged in the reactor vessel. The four-blade impeller connected with the bottom part of the vertical axis and TiO₂ nanotubes/Ti meshes is automatically rotated by the inflow. The revolution speed of the self-rotating body is dependent on the input flow-rate into the reactor vessel, as measured by the tachometer (EE-2N, KONEX, Japan). Due to the above properties, this system can achieve multi-functional advantages, automatic stirring aqueous contaminant as well as effective and utilizing UV light.

The light source used was a 1000 W xenon lamp (Oriel, USA), which was filtered through a 10-cm IR filter. The light emission was above the wavelength of 300 nm, and the irradiated light intensity was determined to be ca. 68 mW cm⁻² (300–400 nm, measured at 65 cm from the center of the light source) using a portable radiometer (UM-360, MINOLTA, Japan). Furthermore, the light intensity absorbed by the TiO₂ seemed to be slightly lower than the irradiated intensity, due to losses by reflection and absorption at the window and in the water.

The structural morphology and the crystal phase of nanotubular TiO₂/Ti were investigated using scanning electron microscopy (SEM, Hitachi S-4700, Japan), and were determined by X-ray diffraction (XRD, Miniflex, Rigaku, Japan; k = 0.89, lambda = 0.15418 for Cu Kα X-ray, 30 kV, 15 mA, respectively. The zeta potential (surface charge) of the sample was measured by an electrophoretic method [30,31] using a commercial instrument (ELS-8000, Otsuka Electronics, Japan) and the concentration of hexavalent chromium (Cr(VI)) was analyzed colorimetrically using UV/Visible
spectrometry (SCINCO, S-3150, Korea) by a 1.5-diphenylcarbazide method [32,33].

3. Results and discussion

3.1. Characterization of anodized TiO\(_2\) nanotubes on Ti mesh

In related studies, the morphology of prepared TiO\(_2\) nanotubes varied noticeably according to the anodizing electrolyte, applied electrical condition, and bath temperature [8–11,28], showing the feasibility of using self-grown TiO\(_2\) nanotubes made from Ti substrates anodized under various conditions. Fig. 2 shows SEM images of TiO\(_2\) nanotubes arrays used as the immobilized photocatalyst. Prior to measurement, a sample area of 100 cm\(^2\) was randomly divided into three pieces of top (A), middle (B) and bottom side (C), respectively, and morphological properties were characterized. As shown in Fig. 2, the anodized TiO\(_2\) grows perpendicular to the Ti mesh substrate forming a nanotubular shape. It is apparent from the top and side view that the TiO\(_2\) layers consist of nanotube arrays, having a length of approximately 6.5–7.0 \(\mu\)m, diameter of 55–60 nm and wall thickness of 10–20 nm. The length and wall thickness of TiO\(_2\) nanotubes varied considerably, depending on the anodizing electrolyte and temperature, due to the variation of the wet chemical etching rate. Porous structures are formed during anodization through two processes: field-enhanced oxidation and field-enhanced oxide dissolution. Furthermore, solid state sintering is likely to take place at the elevated temperatures, a process which leads to grain growth, densification, and ultimately the collapse of the structures. These changes are more remarkable during the phase transformations which often accompany bond-breaking and enhanced mass transport [34].

The measured XRD spectra of the samples, divided into three pieces of those like SEM measurements, are shown in Fig. 3. All of the as-deposited samples were found to be amorphous, while those annealed in dry oxygen at ambient temperature supported the formation of a crystalline phase. The samples were applied to thermal treatment at 450 °C which is consisted of anatase phase. The diffraction peaks at about 2\(\theta\) = 25.4° (101), 48° (200), 53° (105) and 76° (215) can be indexed to the anatase phase of TiO\(_2\). Thus, it can be concluded that the anatase phase appeared after annealing at 450 °C for 2 h. The other peaks at 2\(\theta\) = 35.1° (100), 37.8° (002), 41° (111), 52.9° (102), 63° (110), and 71° (107) can be attributed to the Ti substrate [28,29].

TiO\(_2\) surface has been reported in the literature to behave as a diprotic acid after hydration of the surface functional groups [35]. The surface charge of TiO\(_2\) is a function of the crystal types and solution characteristics such as pH and ionic strength (conductivity). As presented in Fig. 4, the surface charge of the prepared sample was positive at the pH 3 and became more negative with increasing pH. In this result, the zero point charge (p\(zpc\)) was between 3 and 5, which is different from the reported p\(zpc\) of P25 (≈6.8). The distribution of Cr(VI) species in water is a function of pH. Therefore, the neutral chromic acid molecule (H\(_2\)CrO\(_4\)) was dominant at pH values less than 2, while the negatively charged species (HCrO\(_4^−\) and CrO\(_4^{2−}\)) were dominant at pH values higher than 2 [21]. Since the p\(zpc\) of the prepared sample was determined to be between 3 and 5, the surface of TiO\(_2\) nanotubes was more positively charged at pH 3. A neutral species would exhibit little electrostatic attraction for a positive/negative charged surface. At higher pH than p\(zpc\), the negatively charged species (HCrO\(_4^−\) and CrO\(_4^{2−}\)) would be repelled from the negatively charged TiO\(_2\), and thus significantly decreased Cr(VI) reduction efficiency at higher pH ranges.

3.2. The relationship of rotating speed to inflow rate and hydraulic retention time (HRT) in the self-rotating photocatalytic reactor

In this experiment, hydraulic retention time (HRT) is defined as the time \(t\) that a water remains in the photocatalytic reactor calculated as follows [36]:

![Fig. 1. Schematic diagram of the experimental set up for (a) total photocatalytic reaction system and (b) self-rotating photocatalytic reactor.](image-url)
where $V$ is the volume of reactor (L) and $Q$ is the inlet flowrate (L min$^{-1}$). Hence, both HRT and rotating speed of the TiO$_2$/Ti mesh are determined by the inlet flowrate ($Q$) under the fixed volume of the reactor. Fig. 5 shows the relationship between HRT, inlet flowrate, and the rotating speed of TiO$_2$/Ti meshes in the photocatalytic reactor (Fig. 1b). As the results, changes in rotating speed by inlet flowrate substantially altered the HRT. That is, the inlet flowrate increased with higher rotation speed, as HRT significantly decreased.

### 3.3. Photocatalytic reduction of Cr(VI) with self-rotating TiO$_2$ nanotubes/Ti meshes

As mentioned, Cr(VI) reduction depends on pH condition and is favorable under acidic conditions. The reduction of Cr(VI) by photogenerated electrons can be described as follows:

$$
HRT = \frac{V}{Q}
$$
and Cr(VI) are the nanotubes grown on Ti meshes was significantly increased in the conduction band, the reaction potential of chromium ions as a function of pH, the reduction potential (E° = 1.33 V, E shifts 138 mV per pH unit) is more positive than that of the conduction band of TiO₂[15,16,29]. Generally, the kinetics of the photocatalytic reaction follows a Langmuir–Hinshelwood mechanism in heterogeneous media with initial concentration of target pollutant and dosage of catalyst. Because the initial concentration of Cr(VI) employed was low (38.5 μM), the reaction could be reduced to first order as follows [15,33]:

$$\ln \left( \frac{[\text{Cr(VI)}]}{[\text{Cr(VI)}]_0} \right) = k_{\text{red}}t$$  \hspace{1cm} (3)

where $k_{\text{red}}$ values of the Cr(VI) reduction with $R^2$ of linear regression at the given experimental conditions, $[\text{Cr(VI)}]_0$ and $[\text{Cr(VI)}]$ are the Cr(VI) concentrations at the initial time and time, $t$. As shown in Fig. 6, a series of experiments were conducted with self-rotating TiO₂ nanotubes/Ti meshes (four meshes) at pH 3 and varying rotating speeds ranging from 10 rpm to 150 rpm. In addition, the rate constant ($k_{\text{red}}$) values of Cr(VI) reduction with regression coefficients ($R^2$) for the different rotating speeds, evaluated by linear fitting of the logarithmic plot in Fig. 6, are listed in Table 2. In these results, the extent trend of Cr(VI) reduction was found to positively associated with rotation speed. Cr(VI) reductions ranged up to 90% at 90–150 rpm. Especially, Cr(VI) reduction at 90 rpm was observed to be considerably improved which are reached up to 95% within 240 min. These results probably indicated the self-rotating TiO₂ nanotubes/Ti meshes process transferred from mass transfer-limited to surface reaction-limited, and carrying water was sufficiently provided the Cr(VI) to TiO₂ nanotubes at a rotating speed which was equal to the reduction capacity [37]. Consequently, 90 rpm was selected for the following experiments.

Cr(VI) reduction was investigated with varying number of TiO₂ nanotubes/Ti mesh at a rotation speed of 90 rpm (Fig. 7). As expected, the extent of Cr(VI) reduction was not reduced with the direct UV irradiation (without TiO₂/Ti) and effective with increasing numbers of rotating TiO₂/Ti meshes. Where two-rotating Ti meshes were applied, the reduction efficiency of Cr(VI) was a relatively lower because of the small amount of TiO₂ formation on the Ti substrate. In other words, the dosage of nanotubular TiO₂ was insufficient to obtain the efficient reduction of Cr(VI). However, where more than four-rotating Ti meshes were applied, the quantities of TiO₂ nanotubes grown on Ti meshes was significantly increased and promoted greater Cr(VI) reduction at the same rotation speed. In consequence, the reduction of Cr(VI) was determined as up to 95% within 120 min (8 meshes), 180 min (6 meshes), and 240 min (4 meshes), respectively. In addition, the final reduction efficiencies and the rate constant values of Cr(VI) with regression coefficients ($R^2$) for varying number of Ti meshes are summarized in Table 3.

$$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr(III)} + 7\text{H}_2\text{O}$$  \hspace{1cm} (2)

### Table 2

Photocatalytic reduction efficiency, and first-order rate constant of Cr(VI) reduction for various numbers of self-rotating TiO₂ nanotubes/Ti meshes ($[\text{Cr(VI)}]_0 = 38.5 \mu\text{M}, \text{pH 3 adjusted with HCl}$, number of TiO₂/Ti mesh: 4).

<table>
<thead>
<tr>
<th>Rotating speed (rpm)</th>
<th>% Cr(VI) reduction (240 min)</th>
<th>$k_{\text{red}} \times 10^3$ (min⁻¹)</th>
<th>Regression coefficients ($R^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>66.8</td>
<td>4.5</td>
<td>0.989</td>
</tr>
<tr>
<td>30</td>
<td>78.7</td>
<td>6.1</td>
<td>0.984</td>
</tr>
<tr>
<td>60</td>
<td>95</td>
<td>15.3</td>
<td>0.967</td>
</tr>
<tr>
<td>90</td>
<td>≥ 95 (Within 120 min)</td>
<td>11.9</td>
<td>0.978</td>
</tr>
<tr>
<td>120</td>
<td>≥ 95 (Within 180 min)</td>
<td>9.1</td>
<td>0.938</td>
</tr>
<tr>
<td>150</td>
<td>93</td>
<td>9.1</td>
<td>0.938</td>
</tr>
</tbody>
</table>

### Table 3

Photocatalytic reduction efficiency, and first-order rate constant of Cr(VI) reduction for various numbers of self-rotating TiO₂ nanotubes/Ti meshes ($[\text{Cr(VI)}]_0 = 38.5 \mu\text{M}, \text{pH adjusted with HCl, rotating speed: 90 rpm}$).

<table>
<thead>
<tr>
<th>Number of TiO₂/Ti meshes</th>
<th>% Cr(VI) reduction</th>
<th>$k_{\text{red}} \times 10^3$ (min⁻¹)</th>
<th>Regression coefficients ($R^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>≤5</td>
<td>N.A.*</td>
<td>N.A.*</td>
</tr>
<tr>
<td>2</td>
<td>≥95 (Within 240 min)</td>
<td>3.4</td>
<td>0.996</td>
</tr>
<tr>
<td>4</td>
<td>≥95 (Within 240 min)</td>
<td>15.3</td>
<td>0.967</td>
</tr>
<tr>
<td>6</td>
<td>≥95 (Within 180 min)</td>
<td>23.9</td>
<td>0.958</td>
</tr>
<tr>
<td>8</td>
<td>≥95 (Within 120 min)</td>
<td>40.6</td>
<td>0.984</td>
</tr>
</tbody>
</table>

* Not available.
4. Conclusions

This study focused on a self-rotating photocatalytic system for aqueous Cr(VI) reduction on TiO_2 nanotubes on Ti meshes. The self-rotating photocatalytic water treatment system consisted of a vertical axis attached to various number of TiO_2/Ti meshes with impellers at the bottom, which was submerged in the reactor vessel and automatically rotated by the in-flow. The revolution speed and hydraulic retention time (HRT) were significantly influenced by the in-flowrate. Especially, the photocatalytic Cr(VI) reduction efficiency showed better performance at 90 rpm. In addition, Cr(VI) reduction was found to be more effective in the presence of a greater number of TiO_2/Ti meshes. This result indicated that self-rotating TiO_2/Ti meshes transferred from a mass transfer-limit reaction to a surface limited reaction, and carrying aqueous Cr(VI) was sufficiently provided to TiO_2 nanotubes which was enough to the reduction capacity.

For the advanced photocatalytic water treatment system, more detailed studies are needed in order to enhance the stability and treatability of TiO_2 under severe conditions, such as high turbidity, long term evaluation and applications of new emerging contaminants.

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References