

# Lifetime and regeneration of immobilized titania for photocatalytic removal of aqueous hexavalent chromium

Seree Tuprakay\*, Winai Liengcharernsit

*Environmental Engineering Department, Kasetsart University, 50 Phaholyothin Rd., Chatuchak, Bangkok 10900, Thailand*

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## Abstract

Immobilized titania (TiO<sub>2</sub>) batch reactors reduced hexavalent chromium (Cr(VI)) in the form of potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) to trivalent chromium (Cr(III)) in aqueous solution at pH 3 under 171 W/m<sup>2</sup> light intensity. The light source was a 125-W ultraviolet (UV) lamp. The Cr(VI) reduction showed zero-order kinetics ( $k_0$ ), while the Cr(VI) adsorption fitted with first-order kinetics ( $k_{1st}$ ). Adsorption capacity increased with increasing initial Cr(VI) concentration, and the area of immobilized TiO<sub>2</sub> limited the reduction efficiency. The lifetime of fresh immobilized TiO<sub>2</sub> was approximately 14 h. In addition, the regeneration of TiO<sub>2</sub> with 3 M sodium hydroxide (NaOH) was necessary to improve adsorption reaction.

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*Keywords:* Lifetime; Regeneration; Immobilized titania; Photocatalytic; Cr(VI)

## 1. Introduction

Photocatalytic processes are being considered as a method for pollutant treatment [1–8] as they can treat metal ions in industrial wastewater (Hg(II), Pb(II), Cd(II), Ag(I), Ni(II), and Cr(VI)) [9]. These processes use semiconductors such as TiO<sub>2</sub>, SnO<sub>2</sub>, WO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, ZnO, and CdSe, etc. [6,10]. TiO<sub>2</sub> has received the most interest because of its photocatalytic activity, conservative nature, low cost [11], low toxicity, and high stability to light illumination [12]. TiO<sub>2</sub> illuminated with UV light has highly reductive electrons [10]. The reduction converts a variety of inorganic compounds, such as dichromate (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>), to less hazardous substances (reduces Cr(VI) to Cr(III)), which are easier to dispose of or recycle [10,13]. Reactors with a suspension of TiO<sub>2</sub> powder have been widely researched, but a difficult and costly separation step is required after the purification [6,13]. The penetration depth of UV light is also limited in reactors with a suspension of TiO<sub>2</sub> [9,14]. TiO<sub>2</sub> immobilized on a supporting

medium could eliminate the above problems [1,2,5–9,13–16] and reduce operating costs if the immobilized TiO<sub>2</sub> could be reused many times or used for a long period [14,17].

The objective of this research was to study the lifetime and regeneration of immobilized TiO<sub>2</sub> for removal of Cr(VI) in aqueous solution. For this purpose, batch experiments were conducted to study the main parameters, effect of usage time, repeated regeneration, and initial concentrations, on reduction and adsorption of the immobilized TiO<sub>2</sub> reactor.

## 2. Materials and methods

### 2.1. Apparatus

A UV lamp (Philips HPR 125 W) was placed about 5 cm above the reactor containing immobilized TiO<sub>2</sub> that was fixed on the top of the polyester resin (Polylite FG387) (shown in Fig. 1). The batch photoreactors were circular trays of 9.5 cm diameter. The lamp generated 300–400 nm wavelength, and illumination was carried out with UV light intensities of 171 W/m<sup>2</sup> (UV Powermeter: 25.36-3, Sen Lights Corpora-

\* Corresponding author. Tel.: +66 1 2310 8577 8x207; fax: +66 1 2310 8579.

E-mail address: seree4008@ram1.ru.ac.th (S. Tuprakay).

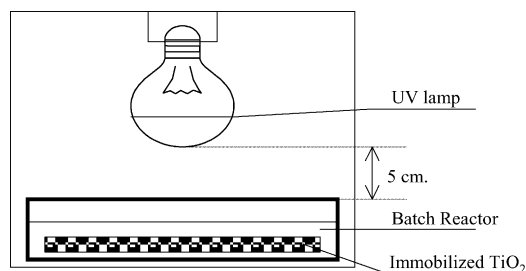


Fig. 1. Batch reactor used in study.

tion, Japan). The lamp and reactor were placed inside a dark box, which was painted black so that no stray light could enter the reactor.

## 2.2. Chemical substances

TiO<sub>2</sub> (UNILAB) photocatalyst was used in the experiments. Stock solution of Cr(VI) was prepared by dissolving analytical grade K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (UNILAB) in distilled water, with H<sub>2</sub>SO<sub>4</sub> and NaOH used for pH adjustment.

## 2.3. Chemical analysis

Samples were analyzed for Cr(VI) using a 1,5-diphenylcarbazide (BDH) colorimetric method [18,19], reading the absorbance at 540 nm in acid solution with a spectrophotometer (Spectronic Genesys 5, Milton Roy, New York). Total chromium was determined using an atomic absorption spectrometer (Perkin-Elmer, Model Analyse100). The difference in concentrations between the total chromium and Cr(VI) was taken as the concentration of Cr(III) [20].

## 2.4. TiO<sub>2</sub> immobilization

The support material was the polyester resin, POLYLITE FG-387, which has excellent chemical resistance to acid, alkali, and high temperature. POLYLITE FG-387 is rapidly cured with MEKPO/Cobalt system, and can be air-dried. TiO<sub>2</sub> was adhered onto the polyester resin in circular trays (about 9.5 cm diameter) [1,2]. The TiO<sub>2</sub> particles are fixed in such a manner that half of the particle surface is accessible for the UV light. TiO<sub>2</sub> powder was poured onto the polyester resin and oven dried at 55–70 °C for 4–5 h. After standing at room temperature overnight, the reactor was washed with a strong stream of water to remove excess powder. Pictures were taken of the surface morphology of the immobilized TiO<sub>2</sub> by scanning electron micrograph (SEM, JEOL Japan).

## 2.5. Experiments

This study used the batch technique to obtain data. A 40 mL cross-flow reactor was used at room temperature and

the radiation density flux on all the surface areas was assumed to be constant for each run. Prior to each experiment, the lamp was preheated for 30 min to obtain a constant light intensity. Before each experiment, the immobilized TiO<sub>2</sub> batch reactor was rinsed with distilled water and run in darkness for 20 min. The pH value of the solution was adjusted to 3.0. The following experiments were carried out:

### 2.5.1. Experiment 1

The effect of initial Cr(VI) concentration and usage time: initial Cr(VI) concentration was studied at 5, 25, and 50 ppm, and usage time of immobilized TiO<sub>2</sub> was studied from 0 to 34 h (2 h/batch).

### 2.5.2. Experiment 2

The effect of regeneration solution concentration. This work used NaOH as a regeneration solution [21]. NaOH concentrations of 0.01, 0.50, 1.00, and 3.00 M were tested on an immobilized TiO<sub>2</sub> reactor used in Section 2.5.1 with 5 ppm initial Cr(VI) concentration and determined total chromium in leachate with AAS.

### 2.5.3. Experiment 3

The effect of regeneration. The used TiO<sub>2</sub> was regenerated up to three times by washing with NaOH [21] for 1 h and reused as in Section 2.5.1.

## 3. Results and discussion

### 3.1. Surface morphology

Fig. 2 shows the SEM micrograph obtained of the immobilized TiO<sub>2</sub> on the polyester resin surface. The rough and nonporous surface of the TiO<sub>2</sub> is clearly shown, and that the polyester resin was half-covered by TiO<sub>2</sub>.

### 3.2. Effect of initial Cr(VI) concentration and usage time of immobilized TiO<sub>2</sub>

These factors affected reduction and adsorption as follows.

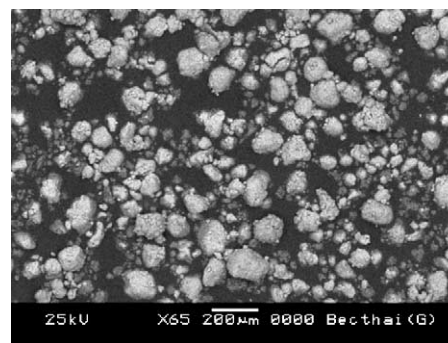


Fig. 2. SEM picture of immobilized TiO<sub>2</sub> on polyester resin.

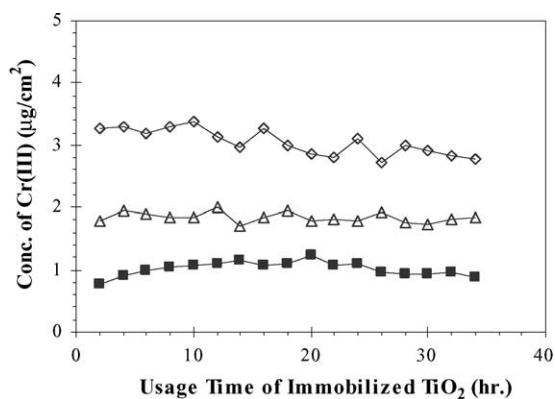
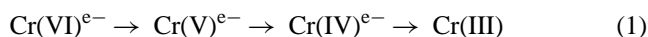


Fig. 3. Effect of usage time of immobilized TiO<sub>2</sub> on reduction by concentration of Cr(III) (µg/cm<sup>2</sup>). Initial Cr(VI) concentrations (■) 5 ppm, (◇) 25 ppm, and (△) 50 ppm, at pH 3, room temperature, and illuminated at 171 W/m<sup>2</sup>.

### 3.2.1. Reduction

The conversion rates of Cr(VI) to Cr(III) for different initial Cr(VI) concentrations up to 25 ppm are shown as the concentration of Cr(III) in Fig. 3. The results show that the minimum was at initial concentration of 5 ppm and the maximum at 25 ppm. At initial, Cr(VI) concentration of 50 ppm electrons was limited on the area of immobilized TiO<sub>2</sub>, and insufficient to reduce high Cr(VI) concentration.

Under UV illumination, electron (e<sup>-</sup>)-hole (h<sup>+</sup>) pairs were produced and the three-electron reaction of Cr(VI) reducing to Cr(III) occurred, while the conjugate anodic reaction was the oxidation of water to oxygen (equations (1)–(3)). Cr(VI) reduction probably occurs via three subsequent one-electron transfer processes, ending in Cr(III), the stable final product [22–27]:



The overall reaction at pH 3 is:



At low initial Cr(VI) concentration (5 ppm), the photocatalytic reaction produced a green deposit on the TiO<sub>2</sub> surface, which corresponded to Cr(OH)<sub>3</sub> (shown in Fig. 4a). Mean-

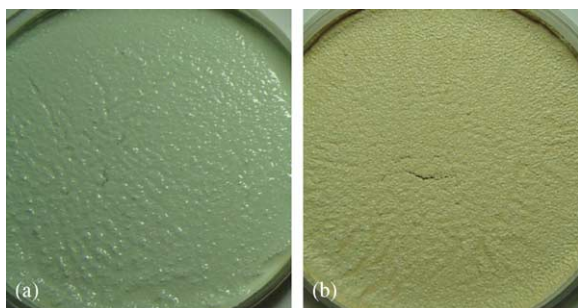


Fig. 4. Surface of immobilized TiO<sub>2</sub> reactor. (a) Low initial Cr(VI) concentrations, green deposit on the TiO<sub>2</sub> surface. (b) High initial Cr(VI) concentrations, yellow deposit on the TiO<sub>2</sub> surface.

Table 1

The  $k_0$  of the reduction of Cr(VI) on immobilized TiO<sub>2</sub>, at pH 3, 171 W/m<sup>2</sup>

Initial Cr(VI) concentration (ppm)	Cr(III) concentration (µg/cm <sup>2</sup> )			$k_0$ (ppm/h)	
	Minimum	Mean	Maximum	S.D.	
5	0.771	1.017	1.225	0.111	0.901
25	2.724	3.046	3.371	0.214	2.698
50	1.716	1.839	2.004	0.080	1.629

while, for high initial Cr(VI) concentrations (>25 ppm), a yellow deposit on the TiO<sub>2</sub> surface was observed, which corresponded to Cr(VI) species [21,23,28–30] (shown in Fig. 4b).

For the reaction rate constant, the reduction of Cr(VI) fitted a zero-order reaction. The  $k_0$  values are shown in Table 1.

### 3.2.2. Adsorption

As shown in Fig. 5, the amount of chromium adsorbed on immobilized TiO<sub>2</sub> increased with increasing initial Cr(VI) concentration. With an increase in usage time of immobilized TiO<sub>2</sub>, chromium adsorption efficiency decreased until adsorption saturation.

In general, anions adsorb through a ligand exchange reaction favored at low pH, where the surface is positively charged and site hydration is favorable. Considering TiO<sub>2</sub> has a positive charge at pH lower than the zero point of charge (pH<sub>ZPC</sub>), it would be expected that the dichromate species (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>) would be electrostatically bonded to the surface [31,32]. The possible reaction between the dichromate species and active groups at the surface of TiO<sub>2</sub> can be expressed by the following equation:



The reaction rate and half-life of chromium adsorption was different from Cr(VI) reduction, as it fitted a first-order reaction as shown in Table 2.

### 3.2.3. Lifetime of immobilized TiO<sub>2</sub>

Fig. 3 shows that the concentration of Cr(III) was almost constant from 0 to 32 h for the reduction reaction. Mean-

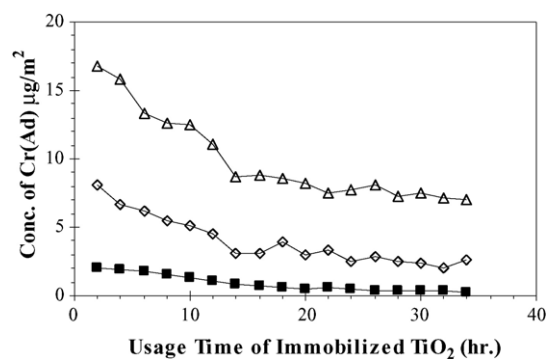


Fig. 5. Effect of usage time of immobilized TiO<sub>2</sub> on chromium adsorption by concentration of chromium adsorption (µg/m<sup>2</sup>). Initial Cr(VI) concentration (■) 5 ppm, (◇) 25 ppm, and (△) 50 ppm at pH 3, room temperature, and illuminated at 171 W/m<sup>2</sup>.

Table 2

The  $k_{1st}$  of adsorption of chromium on immobilized  $TiO_2$ , at pH 3, 171 W/m<sup>2</sup>

Initial Cr(VI) concentration (ppm)	$k_{1st}$ (h <sup>-1</sup> )	$R^2$	$t_{1/2}$ (h)
5	0.0676	0.977	10.251
25	0.0388	0.932	17.861
50	0.0274	0.904	25.292

while, in the adsorption reaction, the concentration of total chromium adsorbed decreased with increasing usage time, and was almost constant after 14 h (Fig. 5). Therefore, for fresh immobilized  $TiO_2$ , the lifetime of the reactor was about 14 h for adsorption and unnecessary to refresh for the reduction reaction.

### 3.3. Effect of NaOH concentration on leachability of adsorbed chromium

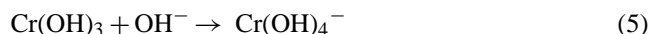
The used immobilized  $TiO_2$  reactors were adsorbed with  $Cr(OH)_3$ , which should be leached from the reactor by treating with NaOH solutions of various concentrations (0.01, 0.50, 1.00, and 3.00 M). It was found that the chromium concentration in leachate from treatment with 3.0 M NaOH solution was highest (Table 3), indicating that washing off with 3 M NaOH was a suitable regeneration method for the deacti-

Table 3

Effect of NaOH concentration on total chromium concentration in leachate, contact time 1 h, 171 W/m<sup>2</sup>

NaOH		Total Cr in leachate (μg)
Concentration (M)	pH	
0.01	11.67	2.60
0.50	12.33	9.32
1.00	12.33	12.16
3.00	12.36	31.48

vated immobilized  $TiO_2$ . This agreed with other research that found that the used  $TiO_2$  could be regenerated by washing off the  $Cr(OH)_3$  with 3 M NaOH (equation (5)) [21,33]:



### 3.4. Effect of regeneration of immobilized $TiO_2$ on reduction and adsorption

Establishment of regeneration methods for used  $TiO_2$  is certainly important from the viewpoint of process economics as  $TiO_2$  could be reused many times or used for a long period. The used immobilized  $TiO_2$  reactors were regenerated by NaOH 3 M for 1 h, after which they were used to treat Cr(VI) at initial concentrations of 5, 25, and 50 ppm.

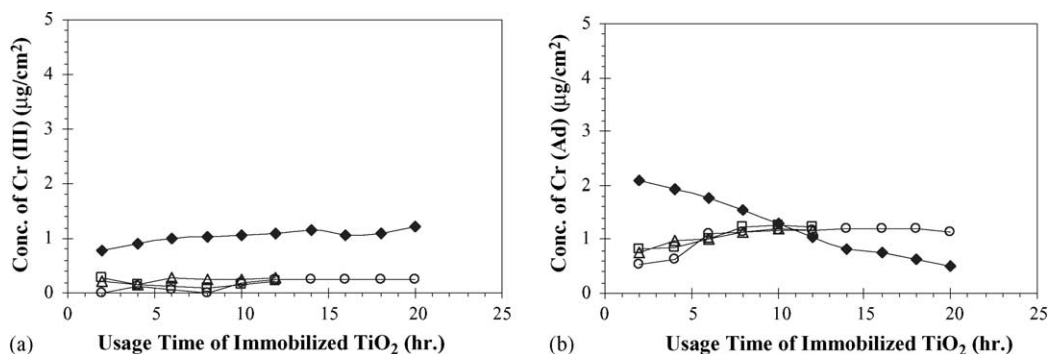


Fig. 6. Effect of usage time and regeneration of immobilized  $TiO_2$  on (a) reduction and (b) adsorption, at initial Cr(VI) concentration 5 ppm, pH 3, 171 W/m<sup>2</sup>, room temperature. (◆) Fresh  $TiO_2$ , (△) first regeneration, (□) second regeneration, and (○) third regeneration.

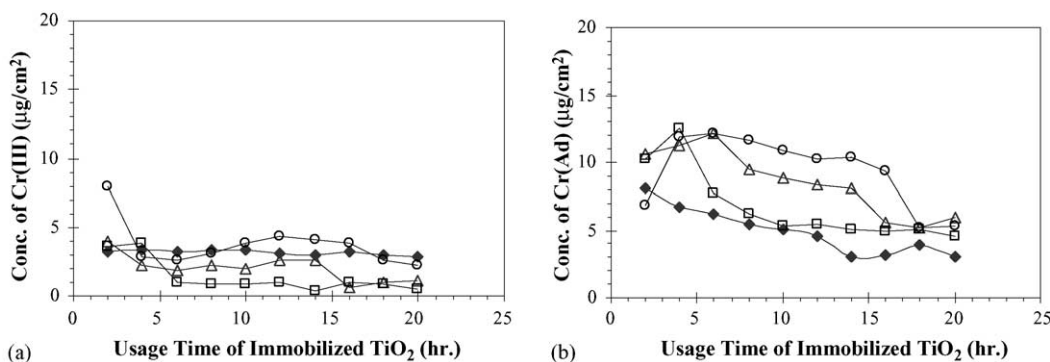


Fig. 7. Effect of usage time and regeneration of immobilized  $TiO_2$  on (a) reduction and (b) adsorption, at initial Cr(VI) concentration 25 ppm, pH 3, 171 W/m<sup>2</sup>, room temperature. (◆) Fresh  $TiO_2$ , (△) first regeneration, (□) second regeneration, and (○) third regeneration.



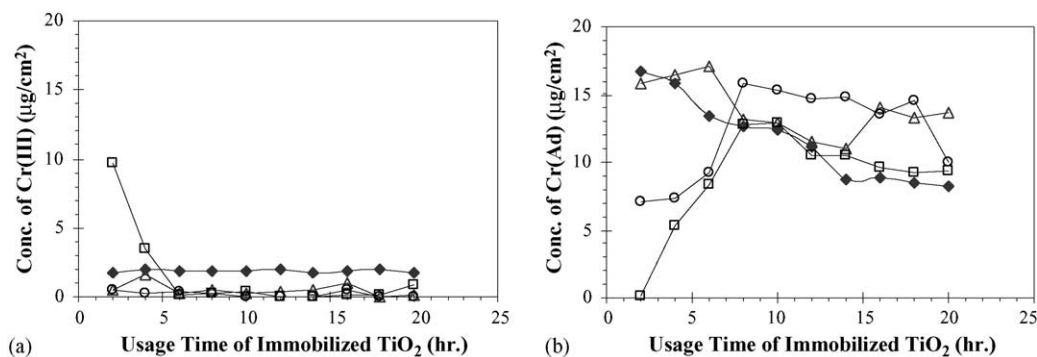


Fig. 8. Effect of usage time and regeneration of immobilized TiO<sub>2</sub> on (a) reduction and (b) adsorption, at initial Cr(VI) concentration 50 ppm, pH 3, 171 W/m<sup>2</sup>, room temperature. (◆) Fresh TiO<sub>2</sub>, (△) first regeneration, (□) second regeneration, and (○) third regeneration.

#### 3.4.1. Reduction

The reduction results are shown in Figs. 6a, 7a, and 8a. They indicate that the fresh TiO<sub>2</sub> was more active than regenerated TiO<sub>2</sub> at all initial concentrations studied, and that Cr(VI) can be reduced to Cr(III) in large amounts by fresh TiO<sub>2</sub>.

#### 3.4.2. Adsorption

Figs. 6b, 7b, and 8b show the adsorption of chromium on regenerated TiO<sub>2</sub> at initial concentrations of 5, 25, and 50 ppm, respectively. These results show that the regenerated TiO<sub>2</sub> can adsorb chromium more than the fresh TiO<sub>2</sub>.

### 4. Conclusions

TiO<sub>2</sub> is able to catalyze the reduction of Cr(VI) to Cr(III) in the presence of UV-light and the following summarizes the most important findings of this research. High reduction capacity was obtained at 25 ppm initial Cr(VI) concentration under 171 W/m<sup>2</sup> light intensity. The amount of chromium adsorbed on immobilized TiO<sub>2</sub> increased with increasing initial Cr(VI) concentration. The lifetime of fresh TiO<sub>2</sub> was about 14 h for adsorption and it was unnecessary to regenerate TiO<sub>2</sub> for the reduction reaction. The reaction rate constant of reduction and adsorption fitted zero- and first-order reactions, respectively. To overcome the degeneration of immobilized TiO<sub>2</sub>, NaOH of 3.00 M concentration is suggested as a suitable solution for regenerating TiO<sub>2</sub> immobilized onto polyester resin. The fresh TiO<sub>2</sub> was more active in reduction of Cr(VI) to Cr(III) than regenerated TiO<sub>2</sub>, while the regenerated TiO<sub>2</sub> could adsorb chromium more than fresh TiO<sub>2</sub>.

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