ORIGINAL ARTICLE

Acid and alkali extraction of trivalent chromium from titanium dioxide surface

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Abstract

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In this work various experimental conditions to extract chromium from titanium dioxide surface using acid and alkali reagents were studied. The effect of type of reagents, concentration of reagents and solid-liquid ratio were investigated. It was found that the chromium extraction using acid reagent provided the higher recovery efficiency than that using alkali reagent. The maximum achievable of chromium extraction (100%) can be found in many experimental conditions using either nitric or sulfuric acids as extraction reagents. The solid-liquid ratio also played a major role in extracting chromium in which the extraction of chromium increased with decreasing solid-liquid ratio. The results also showed that percentage of chromium recovery was increased with increasing of nitric concentration. On the contrary, this maximum recovery percentage was reduced with the rising of sulfuric concentration. Findings from this study could also provide the beneficial information for extraction of other heavy metals from titanium dioxide surface.

Key words : heavy metal, recycling, extraction, leaching, titanium dioxide, photocatalysis

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บทคัดย่อ

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การสกัดด้วยกรดและด่างของไตรวาเลนซ์โครเมียมจากผิวของไททาเนียมไดออกไซด์

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การศึกษานี้เป็นการทดลองสภาวะต่าง ๆ ในการสกัดไตรวาเลนซ์โครเมียมจากผิวของไททาเนียมไดออกไซด์โดยใช้สารสกัดเป็นกรดและด่าง โดยศึกษาถึงผลของชนิดของสารสกัด ความเข้มข้นของสารที่ใช้สกัด และอัตราส่วนของของแข็งต่อของเหลว จากการทดลองพบว่าการใช้กรดเป็นสารสกัดจะให้ประสิทธิภาพในการสกัดได้สูงกว่าการใช้ด่างเป็นสารสกัด กรดที่ให้ประสิทธิภาพสูงสุดที่สามารถสกัดโครเมียมซึ่งคิดเป็น 100% นั้นได้แก่ กรดซัลฟูริก และกรดไนตริก อัตราส่วนของของแข็งต่อของเหลวนั้นเป็นปัจจัยที่สำคัญมากต่อประสิทธิภาพในการสกัดโครเมียมโดยประสิทธิภาพในการสกัดจะเพิ่มขึ้นถ้าค่าของอัตราส่วนของของแข็งต่อของเหลวนั้นลดลง ส่วนผลของความเข้มข้นของสารสกัดนั้น พบว่าในกรณีของกรดไนตริก ประสิทธิภาพในการสกัดโครเมียมจะเพิ่มขึ้นถ้าความเข้มข้นของกรดไนตริกเพิ่มขึ้น ซึ่งตรงข้ามกับการใช้กรดซัลฟูริก โดยประสิทธิภาพในการสกัดโครเมียมจะลดลงหากเพิ่มความเข้มข้นของกรดซัลฟูริก ผลที่ได้จากการศึกษานี้เป็นข้อมูลที่จะเป็นประโยชน์สำหรับการสกัดโลหะหนักชนิดอื่น ๆ จากผิวของไททาเนียมไดออกไซด์ได้

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Photocatalysis is a novel technology for environmental abatement. As an efficient means for pollution treatment, this technology is widely investigated to remove organic and inorganic contaminants from water and wastewater. The most suitable catalyst for photocatalysis is titanium dioxide, TiO_2 (Rajeshwar and Ibanez, 1997). Recently, a corpus of work has already appeared in the use of TiO_2 for the mineralization of contaminated stream (Chen and Ray, 2001). Whilst organic pollutants have received much of the attention, the inorganic pollutants that have been photodegraded by TiO_2 are fewer in variety. Many previous studies (Lin *et al.*, 1993; Chenthamarakshan *et al.*, 2000; Ku and Jung, 2001; Kajitvichyanukul and Vatcharenwong, 2003) show that Cr(VI) can undergo photocatalytic reduction and deposit on the surface of titanium dioxide. Our approach in this study is to dislodge this chromium and regenerate the catalyst by acid and alkali extraction. This process is expected to be effective for chromium removal; however no research goes in-depth in this area.

This extraction technique is used widely in leaching metals from ore (Fallman, 2000; Vardar *et al.*, 1994) and from furnace dust (Xia and Pickles, 1999). For acid leaching, the acidic reagents widely used include sulfuric, nitric and hydrochloric acid (Fallman, 2000). Sodium hydroxide is the extinguishing reagents for alkali leaching. In this paper, the applied techniques of acid and alkali extraction were used to extract Cr(III) from TiO_2 surface for chromium recovery purpose.

Materials and Methods

Titanium dioxide was obtained from photocatalysis process as described in previous study (Kajitvichyanukul and Vatcharenwong, 2003), which is used for chromium removal from contaminant wastewater. Other chemicals were reagent grade or better and were used as received. The experimental apparatus is shown in Figure 1. Titanium dioxide powder and the leach reagent corresponding to a solid-liquid ratio in mass-volume unit as 1/20 or 1/50 was mixed and placed

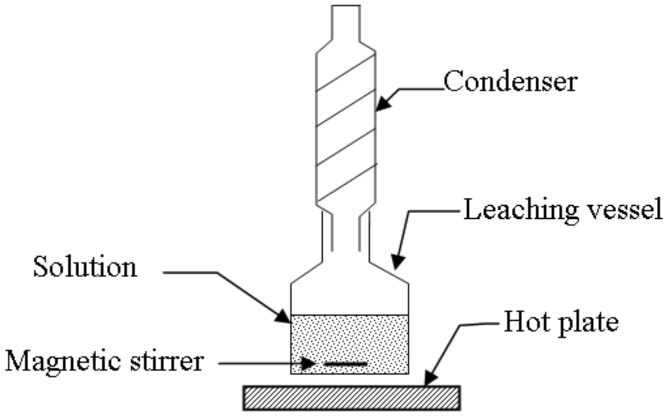

Figure 1. Experimental apparatus of chromium extraction

onto the hot plate. A condenser was used to keep the acid or alkali concentration constant by condensing the water vapor back into the vessel. Strong agitation was maintained to prevent particle agglomeration. No samples were taken during the reaction period. After extraction period, the hot plate was switched off and the reaction vessel was taken off for cooling. The solution was filtered and then analyzed using inductive coupled plasma to determine concentration of extracted chromium.

The studied acidic reagents, sulfuric and nitric acids were purchased from Merck. The alkali reagent was soda ash. The concentrations for each reagent were varied 5 M, 10 M and concentrated solution with the exception of sodium hydroxide in which no experiment for the concentrated reagent was conducted. The leaching time varied from 30 minutes to 3 hours to get the leaching profile.

Results and Discussion

Chromium preparation for extraction

As mentioned in experimental part, chromium in this study was to be extracted from titanium dioxide surface, which was the solid resulting from photocatalysis process. In our previous study (Kajitvichyanukul and Vatcharenwong, 2003), the optimum condition of Cr(VI) reduction from wastewater was obtained. This deposited chromium after photoreduction was suspected to be Cr(III). The speciation of chromium after photoreduction was well investigated by our works and previous researchers (Wang *et al.*, 1992). By observing the color change of the TiO_2 particles, the white-colored particles became yellow after adsorption of Cr(VI) and turned to green during the photocatalytic reduction of Cr(VI) to Cr(III). The used TiO_2 particles after photocatalytic reduction of Cr(VI) were analyzed by X-ray diffractrometer, which indicated that the photocatalytic reduction process did not significantly change the morphology and crystal type of TiO_2. Other study (Ku and Jung, 2001) used Electron Spectroscopy for Chemical Analysis (ESCA) to analyze specie of chromium on the titanium dioxide surface. As shown in Figure 2, the peaks of binding energy of chromium were measured to be 572 eV and 584.4 eV, which indicated that chromium on the surface of TiO_2 was Cr(III). It was also reported that chromium(III) deposited on titanium dioxide surface is thought to be $Cr(OH)_3$ as discussed by previous study (Chenthamarakshan *et al.*, 2000). Thus, from this information, Cr(III) was the original form of chromium appearing on the surface of titanium dioxide that was to be extracted for this study.

Extraction of chromium with nitric acid

The reaction between a simple chromium hydroxide, $Cr(OH)_3$, and nitric acid is given as:

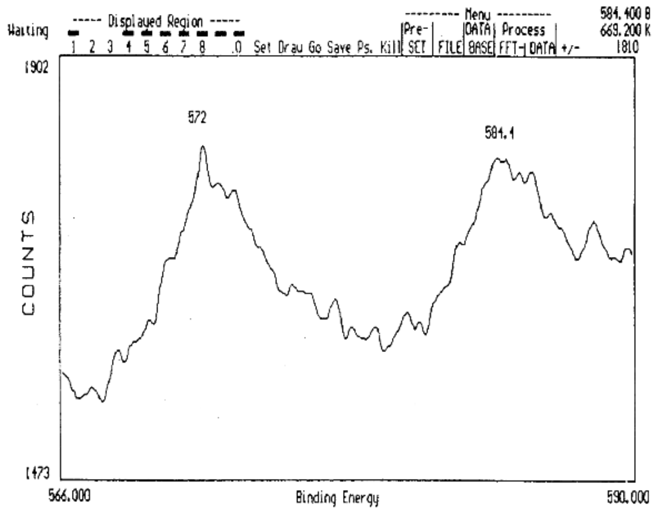

Figure 2. The peaks of the binding energy of chromium was measured to be 572 eV and 584.4 eV by ESCA spectrum

$$Cr(OH)_3 + 3HNO_3 \rightarrow Cr(NO_3)_3 + 3H_2O \qquad (1)$$

However, since the deposition of Cr(III) on titanium dioxide surface was much more complex than given by this equation, the amount of water molecules and the valency level of aqueous nitrates cannot be known with sufficient accuracy to calculate the stoichiometric amount of nitric acid necessary for this reaction. Therefore, the nitric acid and other extracting reagent concentrations were chosen to resemble some typical ones in previous study (Xia and Pickles, 1999).

The results of experiments are given in Table 1.

As can be seen from this Table, the obtainable maximum recovery was nearly 100% for chromium extraction. An example of results from one condition that reaches this maximum efficiency is shown in Figure 3, while the results of minimum recovery condition are shown in Figure 4.

Results from this experiment set show that the chromium extraction increased with increasing of concentration when solid-liquid ration was 1/20. The extraction of chromium increased from 80% to 100% as the solid-liquid ratio was changed from 1/20 to 1/50. Interestingly, with solid-liquid ratio of 1/50, all used nitric concentrations can achieve a maximum chromium recovery.

Table 1. Results for extracting Cr(III) from TiO_2 surface with nitric acid

Extraction Reagents	Concentration (M)	solid-liquid ratio	Time (min)	% Extraction
Nitric acid	5	1:20	60	80
	10	1:20	180	90
	Concentrated	1:20	180	100
Nitric acid	5	1:50	120	100
	10	1:50	60	100
	Concentrated	1:50	60	100

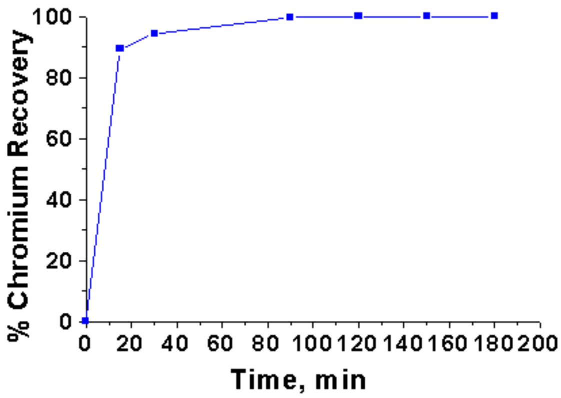

Figure 3. Chromium recovery using 5 M nitric acid, solid-liquid ratio of 1/50

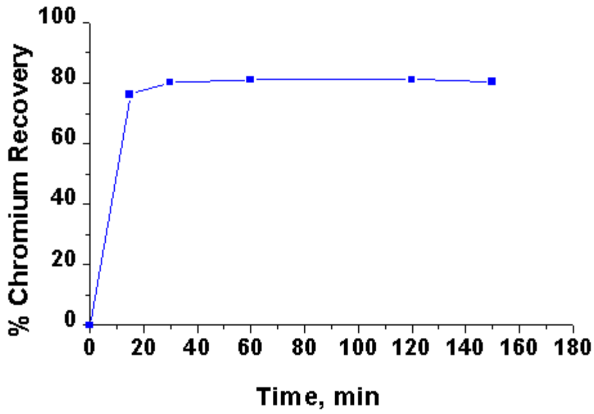

Figure 4. Chromium recovery using 5 M nitric acid, solid-liquid ratio of 1/20

Extraction of chromium with sulfuric acid

The presumed equation of chromium extraction from titanium dioxide surface with sulfuric acid is given as:

$$2Cr(OH)_3 + 3H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 6H_2O \qquad (2)$$

The results of this experiment set are shown in Table 2. Interesting that at higher sulfuric acid concentrations, the recovery of chromium tended to decrease. This explanation was given by previous studies (Verdar, 1994) that it was a result of a decrease in reactivity of sulfuric acid at higher acid concentrations.

The trends of increasing of percentage in chromium extraction with sulfuric acid were the same as those results using nitric acid extraction. It was also the same finding that the extraction of chromium increased with the decreasing of solid-liquid ratio. It was also found that the extraction time to reach the maximum recovery percentage with sulfuric acid (40 minutes) was faster than that required by nitric acid (60-180 minutes).

Extraction of chromium with sodium hydroxide

Sodium hydroxide was another extraction reagent, which was used for leaching of electric arc furnace dust containing a variety of heavy metals (Xia and Pickles, 1999). However, there is no intensive study in this area to identify the product of this extraction. The results of this experiment set are shown in Table 3 and some examples of chromium extraction profile with sodium hydroxide are shown in Figures 5 and 6.

Results from this experiment set also show that the obtainable maximum recovery from

Table 2. Results for extracting Cr(III) from TiO_2 surface with sulfuric acid

Extraction Reagents	Concentration (M)	solid-liquid ratio	Time (min)	% Extraction
Sulfuric acid	5	1:20	40	100
	10	1:20	40	95
	Concentrated	1:20	40	13
Sulfuric acid	5	1:50	40	100
	10	1:50	40	100
	Concentrated	1:50	40	25

Table 3. Results for extracting Cr(III) from TiO_2 surface with sodium hydroxide

Extraction Reagents	Concentration (M)	solid-liquid ratio	Time (min)	% Extraction
Sodium hydroxide	5	1:20	30	60
	10	1:20	30	73
Sodium Hydroxide	5	1:50	30	65
	10	1:50	30	75

chromium extraction using sodium hydroxide was about 75% with 10 M alkali concentration and solid-liquid ratio of 1/50. The chromium recovery efficiency was increased with increasing of alkali concentrations. However, as the experiment time was about 180 minutes, the recovery of chromium did not change appreciably with time and constantly remained in recovery percentage as appeared in the 10-20 minutes extracting duration. Thus, extraction time was not a significant factor for chromium extraction by sodium hydroxide reagent. Obviously, the recovery percentage of chromium with sodium hydroxide was rather lower than those using acid reagents.

Conclusion

In this research work the extraction of chromium from titanium dioxide surface using acid and alkali reagents was studied. The following was concluded considering the experimental results:

1. The extraction using acid reagents yielded the maximum achievement in chromium recovery with higher percentage than use alkali reagent.

2. The major factors that affect chromium recovery efficiency were type of reagents, concentration of reagents and solid-liquid ratio.

3. The maximum chromium extraction was 100% under the conditions as follows:

3.1 Extraction reagent: 5 M sulfuric acid and solid-liquid ratio of 1/20 or /50

3.2 Extraction reagent: 10 M sulfuric acid and solid-liquid ratio of 1/50

3.3 Extraction reagent: 5 or 10 M nitric acid and solid-liquid ratio of 1/50

3.4 Extraction reagent: concentrated nitric acid and solid-liquid ratio of 1/20 or 1/50

Findings from this research could also

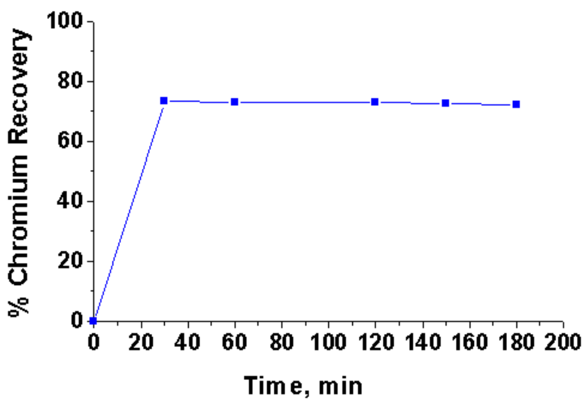

Figure 5. Chromium recovery using 5 M sodium hydroxide, solid-liquid ratio of 1/20

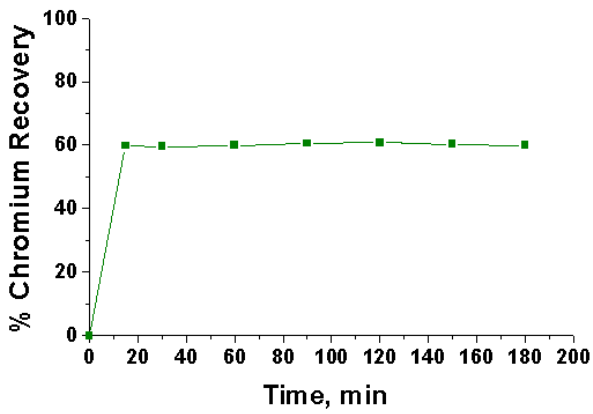

Figure 6. Chromium recovery using 10 M sodium hydroxide, solid-liquid ratio of 1/20

provide beneficial information for the recovery of heavy metals other than chromium from titanium dioxide using in photocatalysis process.

Acknowledgement

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