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Effects of pH and Photocatalyst Concentration on Hexavalent Chromium Removal from Electroplating Waste Water by UV/TiO₂ Photocatalysis

Tedi Hudaya, Alvina Marsha, Eveline Paramita, Shierin and David Andrian
Department of Chemical Engineering, Parahyangan Catholic University,
Ciumbuleuit 94, Bandung 40141, Indonesia

Abstract Chromium electroplating waste water contains toxic Cr⁶⁺ ions which is normally treated by reductive precipitation. However, in Indonesian small-medium scale electroplating industries, these processes are often ineffective since they are rather complicated to apply. Therefore, a batch-wise UV/TiO₂ photocatalysis potentially offers a more effective and easy-to-use process. In this study, waste water containing Cr⁶⁺ similar to real industrial effluents was treated by UV/TiO₂ photocatalysis, in which photogenerated electrons could reduce highly toxic Cr⁶⁺ to relatively harmless Cr³⁺. The photoreactor used in this investigation was a 3-L bubble column photoreactor equipped with a 64 W low pressure UV amalgam lamp (20 W at 254 nm). Preliminary experiments showed 150 min irradiation was required per batch and 3 L min⁻¹ aeration was found to be optimum, resulting approximately 90% removal of hexavalent chromium. The photoreductive treatment was not possible without a hole scavenger (such as EDTA, oxalic acid, citric acid) presence due to the fast recombination of the photogenerated electrons and holes. This investigation, in particular, focused on the two main factors affecting the effectiveness of Cr⁶⁺ photoreductive process which were photocatalyst concentration (varied from 0.5 to 2 g L⁻¹) and pH (in the range of 1-3). Under the experimental conditions, the removal Cr(VI) was between 76.5-94.2%. The most cost effective conditions for the photoreduction of Cr⁶⁺ were found at pH 1 and photocatalyst concentration of 0.5 g L⁻¹ TiO₂.

Key words: Electroplating, hexavalent chromium, UV/TiO₂, bubble-column, photoreactor

INTRODUCTION

Many studies have been conducted to investigate the potential use of photocatalysts in many different areas of interest. For example, the application of thin film titanium oxide for self-cleaning surfaces has been successfully used in Japan (Fujishima *et al.*, 1999). Extensive studies on hydrogen production through water splitting reaction using semiconductor photocatalysts are promising as an alternative energy in the future (Anpo and Takeuchi, 2003). Another major area of photocatalysis study is the use of photocatalysts to oxidize various types of toxic organic pollutants, either in water purification or wastewater treatment processes.

Photocatalysis involves redox reactions of organic or inorganic molecules (Teichner and Formenti, 1985), induced by suitable light irradiation upon a semiconductor particle. Thus, photocatalytic reaction steps can be described as follows (Schiavello, 1988):

- Photogeneration of electron-hole pairs by exciting a semiconductor with radiation of equal or higher energy than the semiconductor band-gap energy

- Separation of electron-hole pairs by surface traps
- Redox reaction between the separated electrons and holes with adsorbed substrates

In other words, some key events of kinetic processes at the surface of the photoexcited semiconductor are: photoexcitation, migration and trapping of the photogenerated electrons and holes, surface charge transfer reaction between trapped electron or hole and adsorbed species and unfavorable electron-hole recombination.

Among several possible semiconductor (ZnO, CdS, WO₃, SrTiO₃, ZnS, TiO₂, SnO₂ and Fe₂O₃) photocatalysts, TiO₂ or TiO₂-based photocatalysts are the most widely used for several reasons. These photocatalysts are non-toxic, inexpensive and have an excellent photoactivity as well as a good chemical stability/durability. In the application of organic pollutant photodestruction, TiO₂ photocatalysts have generally been the most active compared to other semiconductors (Cunningham *et al.*, 1999). The TiO₂ photocatalytic reduction process has been reported as one of the effective methods for the removal of various hazardous

metal ions, such as Hg(II) (Chen and Ray, 2001), As(V)/As(III) (Yang *et al.*, 1999; Lee and Choi, 2002) and Cr(VI) (Ku and Jung, 2001; Testa *et al.*, 2001; Mohapatra *et al.*, 2005; Xu *et al.*, 2006; Rengaraj *et al.*, 2007).

The absorption of photon or light energy at or near the surface of a semiconductor particle can excite the solid semiconductor. Semiconductors are characterized by energetically non-overlapping bands (Pitchat and Fox, 1988). Thus, this photo-excitation means a band-to-band electronic transition, moving an electron from the topmost filled band (valence band) to the closest empty band (conduction band). The difference between energy level of these bands is known as band-gap energy. TiO₂ semiconductor in anatase form has a relatively high energy band gap (3.2 eV), corresponding to irradiation threshold of λ below 387 nm (Pareek and Adesina, 2003). The rutile form of TiO₂ has a slightly smaller energy band gap (3.02 eV) and hence the threshold is 410 nm (Li *et al.*, 2000).

Chromium occurs in two common oxidation states in nature, Cr(III) and Cr(VI). Cr(VI) is highly toxic to most organisms, carcinogenic in 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 (HCrO₄⁻/CrO₄²⁻) and dichromate (Cr₂O₇²⁻), respectively, depending on its concentration and pH. Cr(VI) toxicity is one hundred times higher than that of Cr(III) (Costa, 2003; Yoon *et al.*, 2005). Therefore, the reduction of Cr(VI) to Cr(III) is highly desirable in order to minimize the toxicity level of the waste water. After Cr(VI) reduction, Cr(III) can be separated by precipitation in alkaline solution as Cr(OH)₃ (Loyaux-Lawniczak *et al.*, 2001; Schlautman and Han, 2001).

Cr(VI) is a frequent contaminant in industrial waste water, arising from some industrial processes such as electroplating, leather tanning and paint-making and it has been regulated stringently due to its acute toxicity, carcinogenic action and high mobility in water. In Indonesia, small-medium scale electroplating plants are normally run by small businesses with limited knowledge and resources. Therefore, conventional chemical reductive treatment of Cr(VI) followed by alkaline precipitation is proven not very effective (Sugiharto *et al.*, 2003), yet rather complicated to apply. Since the UV/TiO₂ appears to be an effective technology for heavy metal ions removal from waste water, its application especially in a batch mode in such small scale electroplating business offers a promising outcome. Batch mode operation is very simple to follow and an established SOP (Standard Operating Procedure) can be developed to ensure the success removal of toxic Cr(VI) from the effluent.

Yoon *et al.* (2009) conducted a series of experiments in an attempt for reducing Cr(VI) by UV/TiO₂ photocatalysis. In their experiments, the pH of the solution ranged from 3-9. Their experimental results showed that the photocatalytic Cr(VI) reduction was favorable in acidic conditions, with around 98% of the Cr(VI) could be reduced within 2 h at pH 3. However, the photoreduction efficiencies decreased with increasing pH, ranged only 5-15% at pH 5-9.

Kajitvichyanukul and Changul (2005) reported that the photoreduction of total chromium, including hexavalent and trivalent chromium, was improved with increasing doses of TiO₂ photocatalyst. The 300 ppm chrome waste water used in that study was adjusted to pH 3.

From the photocatalysis point of view, those two parameters are quite important and determining the overall photoreduction and photooxidation rates occurring at the photocatalyst surface. Hence, the aim of this study was to determine the optimal combination of pH (in acidic condition with pH = 3) and TiO₂ photocatalyst concentration which had not been explored in previous investigations using UV/TiO₂ photocatalytic system. However, since those optimal conditions will be used for treating Cr⁶⁺ waste water from typical Indonesian small-medium scale electroplating plants, the process must be as cost-effective as possible.

MATERIALS AND METHODS

Materials: A synthetic waste solution of 50 ppm Cr(VI) was made by dissolving potassium dichromate K₂Cr₂O₇ resembling to chromium containing waste water from a medium scale electroplating plant in Bandung, Indonesia. The photocatalyst used was Merck TiO₂, consists of 99% anatase TiO₂. Citric acid as a hole scavenger was added to the solution, in which the mole ratio of hole scavenger and Cr(VI) used was 1.25:1 (Meichtry *et al.*, 2007). The solution pH was varied between 1-3, meanwhile the TiO₂ concentration ranged between 0.5-2 g L⁻¹.

Photoreactor: Experiments were conducted in a 3 L laboratory scale bubble column photoreactor (Fig. 1). The reactor was equipped with a cooling water jacket to maintain the reaction temperature. The light source used was a 64 W Heraeus Low Pressure UV amalgam lamp and placed in a quartz cylinder. Prior to illumination, the mixture was aerated under dark condition for 30 min to reach adsorption equilibrium. Reaction time was 150 min and 25 mL sample was withdrawn for every 30 min.

Cr(VI) analysis: The concentration of Cr(VI) was followed colorimetrically by spectrophotometry analysis using LW Scientific UV-VIS Spectrophotometer (model

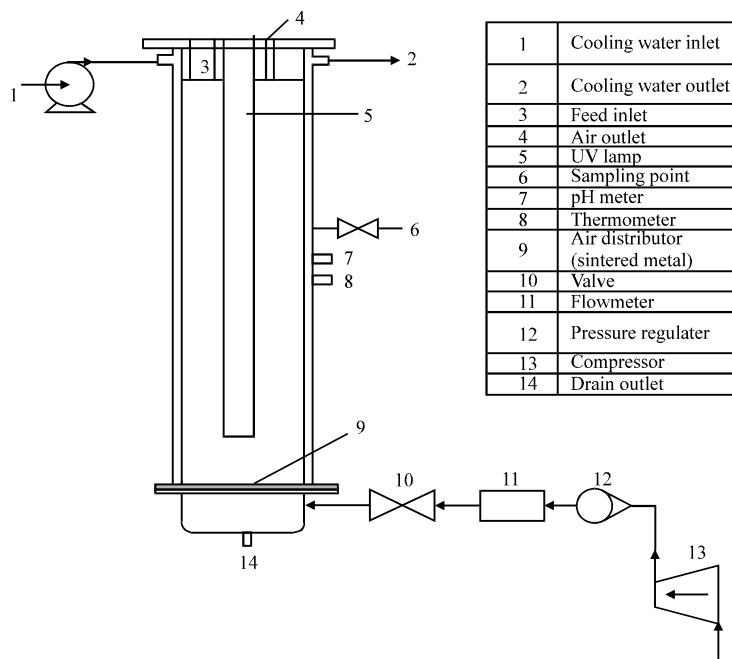


Fig. 1: Schematic diagram of bubble column photoreactor

UV-200 RS). In this spectrophotometric method, each sample was prepared using the Diphenylcarbazide (DPC) solution. DPC solution was made from 250 mg of 1,5-diphenylcarbazide dissolved in 50 mL of acetone (APHA/AWWA/WEF, 1998) and 0.2 N H_2SO_4 and H_3PO_4 were used for pH adjustment.

RESULTS AND DISCUSSION

The experimental results of Cr(VI) reduction with photocatalysis UV/ TiO_2 showed that there was a color changing in the waste solution from yellow to transparent. Initial yellow color indicated the high concentration of hexavalent chromium still remaining in the waste solution, meanwhile the fading yellow color was due to the concentration of hexavalent chromium was gradually reduced. The quantitative result was analyzed by the value of k (pseudo 1st order reduction rate constant) as well as the % removal of Cr(VI).

Preliminary experiments: In a bubble column photoreactor, the mixing of reaction mixture is achieved by using aeration. The photocatalysis is a heterogeneous process in which the photo reduction of Cr(VI) occurs at the surface of the TiO_2 photocatalyst. The aeration rate in one hand affects the rate of mass transfer from liquid bulk phase to catalyst surface significantly. An excellent

mixing of mixture will enhance the photocatalysis process since increasing aeration rate minimizes mass transfer resistance. However, on the other hand the rate of aeration must not be too excessive, because oxygen (an electron scavenger) will compete for the photogenerated electrons which are meant to reduce hexavalent chromium, hence the reduction reaction will be hampered. Therefore, the optimum rate of aeration must be determined in the UV/ TiO_2 system beforehand. Figure 2 shows the reduction rate constants in different aeration rates. Initially, higher aeration rate results in greater Cr(VI) reduction rate constant. It means that the reduction process are faster due to more intimate mass transfer at high aeration rate. However, experimental results show that the Cr(VI) reduction rate constant decreases at aeration rate $4 L min^{-1}$ and hence the optimum aeration is found at $3 L min^{-1}$.

In some preliminary experiments, the photoreduction of Cr(VI) was not possible without the presence of an additive agent, as shown in Fig. 3. The additive agent is named as hole scavenger (such as EDTA, citric acid and oxalic acid). As the photogenerated electrons and holes experience a series reaction with other adsorbed species on photocatalyst surface, at the same time they can also recombine because of the instability of electron and hole which have opposite charge. Electron-hole recombination may greatly reduce the Cr(VI) reduction rate, because it is

thermodynamically favorable. Hole scavengers contribute to minimize the recombination reaction through the binding of produced holes (Meichtry *et al.*, 2007), so that, the photogenerated electrons may be utilized more effectively for reductive purposes.

The measured Cr(VI) reduction rate constants using each hole scavenger are shown in Table 1. EDTA and

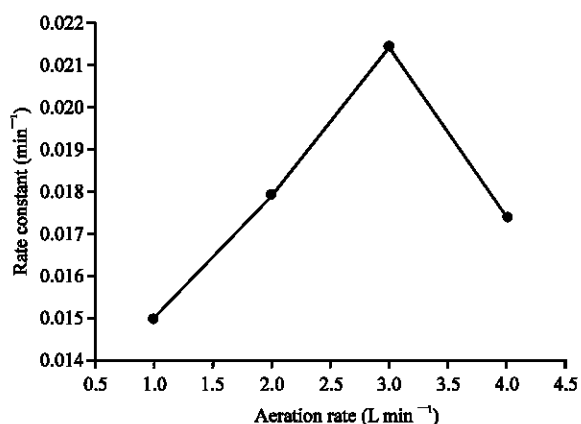


Fig. 2: Cr(VI) reduction rate constants at various aeration rate

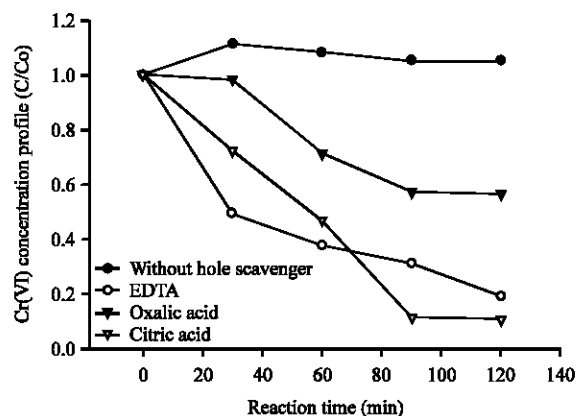


Fig. 3: Photoreduction process of Cr(VI) with and without the assistance of hole scavengers

Table 1: Reduction rate constants for several types of hole scavenger

Type of hole scavenger	Rate constant (minute ⁻¹)
EDTA	0.0142
Oxalic acid	0.0052
Citric acid	0.0191

Table 2: Rate constants and % removals of Cr(VI) in various condition

pH	[TiO ₂] = 0.5 g L ⁻¹		[TiO ₂] = 1 g L ⁻¹		[TiO ₂] = 2 g L ⁻¹	
	Rate constant (minute ⁻¹)	Removal (%)	Rate constant (minute ⁻¹)	Removal (%)	Rate constant (minute ⁻¹)	Removal (%)
1	0.0134	90.86	0.0135	89.09	0.0173	94.19
2	0.0126	81.44	0.0115	78.89	0.0109	76.53
3	0.0092	78.55	0.0085	78.73	0.0095	77.78

citric acid resulted in a much higher reduction rate constant than that of oxalic acid. Since citric acid price is around one third of EDTA, citric acid was then chosen as a hole scavenger throughout the experiments.

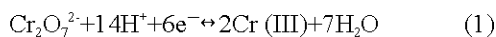
Effect of photocatalyst concentration and pH on the reduction rates: In the following experiments, the effects of photocatalyst concentration and pH on the Cr⁶⁺ reduction effectiveness were determined. Solution pH was varied between 1 to 3, meanwhile TiO₂ concentration ranged from between 0.5 to 2 g L⁻¹. Those variations were chosen in accordance with the previous experiment done by Yoon *et al.* (2009), in which the photocatalytic Cr(VI) reduction was favorable in acidic environment. Moreover, similar results were also found by Slamet *et al.* (2003).

Optimum conditions for Cr(VI) treatment can be determined by evaluating the pseudo 1st order rate constants (Wang *et al.*, 2010) and the (%) removals (Table 2). The rate constants represent how fast the reduction occurs, meanwhile % removals show how much Cr(VI) can be converted to Cr(III).

Based on the experimental results in Table 2, the reduction of the Cr(VI) is significantly affected by the solution pH, because first of all, the pH of the solution affects the surface charge on TiO₂ photocatalyst. The pH value for the zero ionic charge is called point of zero charge (pH_{ZPC}) (Hoffmann *et al.*, 1995). For anatase TiO₂, the point of zero charge is around 6.0-6.4 (Berube and de Bruyn, 1968). Below this point of zero charge, the surface charge of the TiO₂ will be positive and conversely, above this point the surface charge will be negative. Considering the HCrO₄⁻, CrO₄²⁻ and Cr₂O₇²⁻ as the predominant species at medium to low pH values (>2), the photocatalyst surface which have positive charge in the acidic solution will adsorb the Cr(VI) species strongly due to the opposite charge interaction (Yoon *et al.*, 2009) at pH 3. At pH less than 2 the dominant species is neutral chromic acid molecule, H₂CrO₄ which is adsorbed less strongly than the negatively charged species at higher pH.

Interestingly, the reaction rate constants in Table 2 appear to be conflicting with the previously described phenomena. Therefore, there must be another effect of the pH on the complex system. In fact, the pH also significantly affects the Cr(VI) to Cr(III) reduction potential (E⁰_{Cr(VI)/Cr(III)}) and lower pH increases the potential

to be more positive (by 0.13 V/unit pH) than that of the conduction band of TiO₂ (Xu *et al.*, 2004; Cappelletti *et al.*, 2008). Consequently, at low pH, the reduction of Cr(VI) is thermodynamically favorable and hence, greater rate constant and Cr(VI)% removal is observed in the more acidic solution, overweigh the effect of adsorption strengths at various pH. The reduction of Cr(VI) by photogenerated electrons can be described as follows:



Heterogeneous photocatalytic reactions which take place on the catalyst surface, largely depend on physical characteristics of catalyst, such as particle size, surface area, surface defects, surface metal deposits and crystalline phase (Wang *et al.*, 2010). However, the experimental results in Table 2 show that the variation of TiO₂ concentration (at every pH level) does not cause any discernible effects on both rate constant and Cr(VI)% removal. The increasing catalyst concentration may enhance the reaction rates as the photocatalysis process took place at the catalyst surface. Nonetheless, the effect is not reflected from the result of this investigation due to the fact that the concentration of Cr(VI) in the waste solution is relatively very small of 50 ppm compared to a similar study (Kajitvichyanukul and Changul, 2005). In other words, the TiO₂ concentration of 0.5 g L⁻¹ provided sufficient surface area for Cr(VI) adsorption and reduction at that low concentration.

The experiment results in Table 2 show that the reduction of Cr(VI) reaches the maximum rate at pH 1 and 2 g L⁻¹ TiO₂. However, the % removal at pH 1 and 0.5 g L⁻¹ L TiO₂ is just 3% lower than that of 2 g L⁻¹ experiment. Therefore, taking the cost of the photocatalyst into account, it can be concluded that the Cr(VI) reduction is best carried out at pH 1 and TiO₂ concentration of 0.5 g L⁻¹.

CONCLUSION

Preliminary experiments 3 L min⁻¹ aeration was found to be optimum for hexavalent chromium photoreduction in a 3 L batch UV/TiO₂ photoreactor system. The reductive treatment was not possible without a hole scavenger (such as EDTA, oxalic acid, citric acid) presence due to the fast recombination of electrons and holes. Under the experimental range, the Cr(VI) removal was achieved from 76.5-94.2%, under 150 min irradiation by a 64 W UV lamp. The most cost effective condition for the reduction of Cr(VI) was found at pH 1 and 0.5 g L⁻¹ TiO₂.

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