THE SIMULTANEOUS REMOVAL OF CYANIDE AND CADMIUM IONS FROM ELECTROPLATING WASTEWATER USING UV/TIO2 PHOTOCATALYSIS

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ABSTRACT

The simultaneous oxidation of cyanide and reduction of cadmium from electroplating wastewater using UV/TiO$_2$ photocatalysis was investigated in this study. The investigation was performed using a batch-wise 3 L bubble-column photoreactor equipped with a 64-Watt low-pressure ultraviolet (UV) amalgam lamp (20 W at 254 nm). Preliminary experiments were conducted to identify the optimum aeration rate for ensuring the mixing of the catalyst and the wastewater. More specifically, this study focused on the two main factors that influence the effectiveness of oxidative and reductive processes, namely the TiO$_2$ concentration (0.5–2 g/L) and the solution's pH (11–13), at cyanide and cadmium ion concentrations of 50 and 100 ppm, respectively. A sample was taken every 30 minutes for 3 hours, and the cyanide and cadmium ion concentrations were determined using an ion-selective electrode and atomic absorption spectroscopy (AAS), respectively. It was determined that 3 L/min aeration was optimum, resulting in the removal of approximately 80% of the pollutants. A further increase in the aeration rate resulted in a decrease in the % removal rate due to competition between the oxygen and cadmium ions in terms of reacting with the electrons produced by the photocatalyst. An increase in the pH resulted in an increase in both the removal rate and the kinetics due to the high availability of the hydroxide ions needed to form the radical hydroxide that effectively oxidized the cyanide ions. It was observed that an increase in the TiO$_2$ concentration increased both the removal rate and the kinetics until the optimum point, after which the performance of the photocatalyst decreased due to the shielding effect of the UV resulting from the excessive level of TiO$_2$ present in the mixture. Within the experimental range, the best (most effective) condition was chosen based on the pseudo first-order rate constants. The best condition for cyanide oxidation was identified at pH 13 and 1 g/L TiO$_2$ with k_{CN^-} 0.033 min^{-1}, while the reduction of cadmium was found to be optimum at pH 13 and 2 g/L TiO$_2$ with $k_{Cd^{2+}}$ 0.039 min^{-1}.

Keywords: Cadmium; Cyanide; Electroplating wastewater; Photocatalysis; UV/TiO$_2$
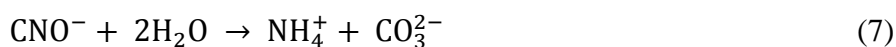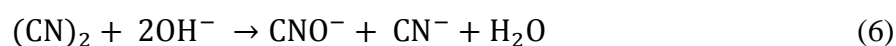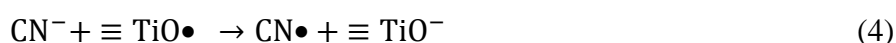
1. INTRODUCTION

UV/TiO$_2$ photocatalysis has been widely known as an alternative for treating wastewater as a tertiary treatment. As a photocatalyst, TiO$_2$ offers a number of benefits due to being stable, inert, relatively cheap, commercially available, and highly photoactive. During the photocatalysis process, ultraviolet (UV) irradiation acting on the TiO$_2$ surface results in the excitation of electrons. Hence, both electrons (e$^-$) and holes (h$^+$) are generated, which then act

as reductors and oxidators, respectively, for the species adsorbed on the catalyst's surface (Nakata & Fujishima, 2012). This process is shown in Equation 1.

$$TiO_2 \xrightarrow{h\nu} TiO_2 + h^+ + e^-$$ (1)

Cyanide (CN⁻) is a highly toxic species that can be found in electroplating wastewater. Cyanide can be completely oxidized into ammonium and carbonate via cyanate as an intermediate (Marugan et al., 2008). The oxidation of cyanide by photocatalysis UV/TiO₂ (Chiang et al., 2003; Marugan et al., 2008) is illustrated in the following reactions:

$$\equiv TiO^- + h^+ \rightarrow \equiv TiO\bullet$$ (2)

$$CN^- + h^+ \rightarrow CN\bullet$$ (3)

$$CN^- + \equiv TiO\bullet \rightarrow CN\bullet + \equiv TiO^-$$ (4)

$$2CN\bullet \rightarrow (CN)_2$$ (5)

$$(CN)_2 + 2OH^- \rightarrow CNO^- + CN^- + H_2O$$ (6)

$$CNO^- + 2H_2O \rightarrow NH_4^+ + CO_3^{2-}$$ (7)

While the holes generated during photocatalysis could serve to oxidize cyanide, the electrons on the other hand could be used to reduce the metal ions adsorbed on the surface of the catalyst. The reduction of cadmium ions (Cd^{2+}) to zero-valent cadmium (Cd(0)) at a pH of 7–11 has previously been investigated by Nguyen et al. (2003). The reduction of cadmium ions is shown in the following reaction:

$$Cd^{2+} + 2e^- \rightarrow Cd$$ (8)

Hole scavengers, which are usually organic species, such as formate ions or methanol, are required for the reduction of cadmium ions alone, in order to minimize the recombination reaction between the photogenerated electrons and holes (Nguyen et al., 2003).

There are other possible methods available for the treatment of heavy metal ions, such as coagulation-flocculation, ion exchange, adsorption, and membrane/ceramic filtration (Acheampong et al., 2010; Nasir & Faizal, 2016). The precipitation and coagulation-flocculation methods are usually considered to be both practical and economical; however, a large volume of sludge is produced as a result of these methods. Adsorption, ion exchange, and membrane/ceramic filtration can effectively remove heavy metals, although the associated material and operational costs are high (Acheampong et al., 2010). As for cyanide ions, oxidation using sulfur dioxide/air, hydrogen peroxide, or alkaline/chlorination is usually used to convert cyanide ions into a less toxic compound (Acheampong et al., 2010). Yet, these methods also have a number of drawbacks, such as the formation of highly toxic intermediates (in the case of alkaline/chlorination), the high volume of sludge produced, and the relatively expensive chemicals required.

The photocatalytic treatment of other metal-cyanide complexes, such as [Cu(CN)₄²⁻] (Barakat, 2004), [Fe(CN)₆³⁻] (van Grieken et al., 2005), [Zn(CN)₄²⁻], and [Cu(CN)₃²⁻] (Ozcan et al., 2012), has previously been performed. However, to the best of the authors' knowledge, the photocatalytic treatment of the cadmium cyano complex has not previously been attempted. In this study, wastewater containing cyanide and cadmium resulting from the cadmium electroplating process (commonly used for aviation turbines) was treated using UV/TiO₂

photocatalysis, which involves the holes and electrons being able to oxidize the cyanide and, at the same time, reduce the heavy metal cadmium to non-soluble zero-valent cadmium. Cadmium, in the presence of excess cyanide ion, is bonded into the tetracyanocadminate complex, $[Cd(CN)_4^{2-}]$ (Hu et al., 2015). This complex is stable in basic condition (essential for preventing the release of extremely toxic HCN gas), as are the cyano complexes of other transition metals (Miltzarek et al., 2002), which renders this kind of pollutant difficult to treat using conventional methods, such as metal precipitation. Furthermore, the photocatalytic technique allows for the simultaneous oxidation of cyanide and reduction of cadmium in a cadmium cyano complex solution, which simplifies the steps needed to treat wastewater. The effect of the pH and the TiO_2 concentration on the removal and reaction kinetics of the $[Cd(CN)_4^{2-}]$ complex was also investigated.

2. EXPERIMENTAL METHODS

2.1. Materials

Three liters of wastewater were introduced into the photoreactor (Figure 1) for each batch of variations. This wastewater was synthetically made based on the real composition of a surveyed wastewater sample obtained from a local cadmium electroplating plant. Potassium cyanide (p.a. Merck) and coarse cadmium granules (p.a. Merck) were used as the main pollutants to be treated in this study. Further, slight amounts of sodium hydroxide and nitric acid were used for pH adjustment purposes. All the species were dissolved in reverse osmosis (RO) water with an initial cadmium concentration of 50 ppm and a total cyanide concentration of 100 ppm. The TiO_2 used as the photocatalyst was Merck 100% anatase.

2.2. Bubble-column Photoreactor and Procedure

The simultaneous reduction and oxidation of the $[Cd(CN)_4^{2-}]$ was performed in a bubble-column photoreactor. The reactor was equipped with a 64-Watt low-pressure UV amalgam lamp (20 W at 254 nm) as the source of UV light. The lamp was protected by a quartz glass sleeve. The aeration required for the mixing was provided by an air compressor, and the aeration flow could be adjusted using a flow meter. The reactor was enclosed in a cooling water jacket in order to prevent the temperature rising above $40^{\circ}C$ due to the abundant heat produced by the UV lamp. A sample of the treated wastewater was taken every 30 minutes during the 3-hour reaction period. Each sample was preserved by adjusting its pH to 12 or higher. The concentrations obtained were then fitted into the pseudo first-order reaction kinetics, as shown in Equation 9 and, in its integrated form, in Equation 10.

$$\frac{dC}{dt} = -k'.C \tag{9}$$

$$\ln\frac{C_o}{C} = k'.t \tag{10}$$

This study was separated into two distinct parts. The first part involved the determination of the optimum aeration rate (pH 11, TiO_2 concentration 1g/L), while the second part involved the observation of the effect of the solution's pH (11 to 13) and the TiO_2 concentration (0.5 to 3 g/L) at the optimum aeration rate. All the experiments were conducted without replication.

2.3. Instrumentation

The free cyanide concentration in the collected samples was measured using a Metrohm ion-selective electrode, while the dissolved cadmium ion concentration was measured using atomic absorption spectroscopy (AAS; Hitachi Z-2300).

3. RESULTS AND DISCUSSION

3.1. Optimum Aeration

Aeration provides the turbulence needed for mixing purposes, as well as serving to minimize the mass transfer resistance. Therefore, at a sufficient aeration rate, the solution was well mixed and the mass transfer resistance was minimized, which in turn enhanced the reaction rate.

Figures 1 and 2 show that increasing the aeration rate from 1 to 3 liters/min caused faster cyanide oxidation and cadmium reduction. However, at an excessive aeration rate of 4 liters/min, a significant decrease in both cyanide oxidation and cadmium removal was observed. The pseudo first-order reaction rate derived from the aeration experiments (presented in Table 1) confirmed that an optimum aeration level was necessary to ensure more effective treatment.
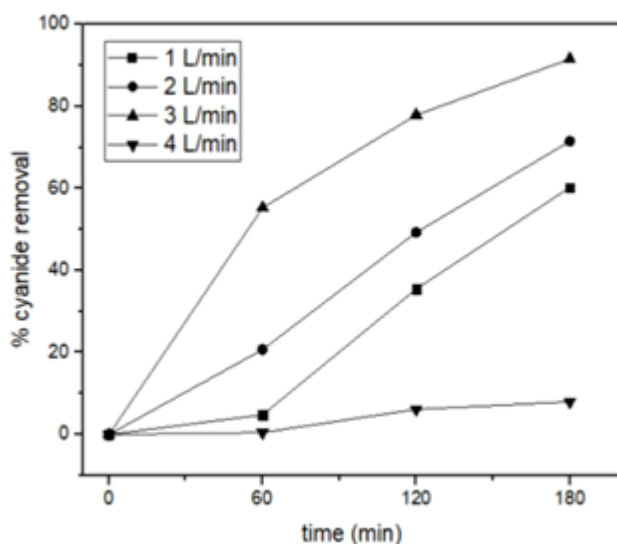

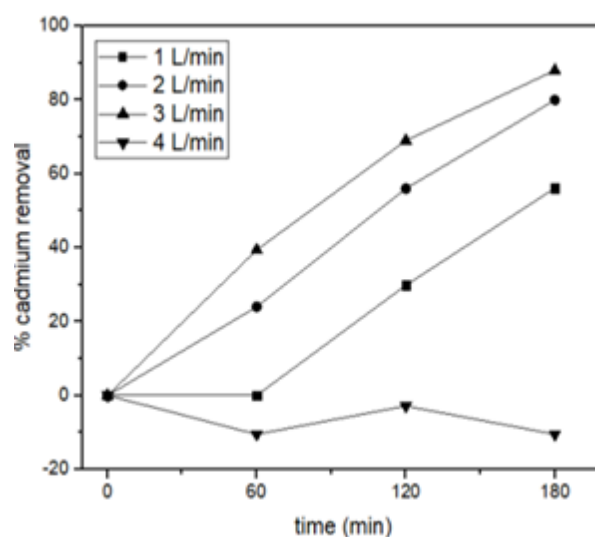Figure 1 Removal of cyanide vs. time at various aeration rates

Figure 2 Removal of cadmium vs. time at various aeration rates

Table 1 Pseudo first-order rate constants for cyanide oxidation and cadmium reduction at various aeration rates

Aeration rate (L/min)	k_{CN^-} [min^{-1}]	$k_{Cd^{2+}}$ [min^{-1}]
1	4×10^{-3}	3×10^{-3}
2	6×10^{-3}	8×10^{-3}
3	13×10^{-3}	11×10^{-3}
4	0,6×10^{-3}	0

In the presence of excess oxygen due to more extensive aeration, the cadmium reduction rate decreased significantly. At a high aeration rate, the dissolved oxygen (known to be good electron scavengers) competed with the cadmium in terms of accepting electrons, which slowed down the cadmium ion reduction. Once the cadmium ions had been reduced, the free cyanide ions were ready for oxidation. At the same time, excessive levels of adsorbed oxygen could react to become hydroxide ions, which would render the TiO$_2$ surface more negative. For the anatase TiO$_2$, the point of zero charge fell within the pH range of 6.0–6.4 (Barakat, 2004), above which the TiO$_2$ surface would become negatively charged. This would make the adsorption of cyanide on the TiO$_2$ surface became much more difficult. The reaction transforming oxygen into hydroxide (Equation 2) is shown in Equation 11.

$$O_2 + H_2O + 2e^- \rightarrow HO^- + HO_2^- \tag{11}$$

Therefore, the optimum aeration rate of 3 L/min had to be applied so that: (i) the solution was well mixed; and (ii) more effective cadmium reduction and cyanide oxidation could be achieved.

3.2. Initial pH and TiO₂ Concentration

In this study, the solution's pH was varied between 11 and 13, while the utilized TiO₂ concentration was varied between 0.5 and 3 g/L. The optimum aeration rate was used. It is essential to work in a basic pH range (preferably above 10), since at lower pHs the cyanide ions could be released as HCN, which is a highly toxic gas.

Figures 3 and 4 generally show the effect of the solution's pH at the same TiO₂ concentration. From both figures, it could be concluded that at a higher pH, the removal rates for both species increased. This finding is in agreement with previously obtained results concerning cyano-metal complexes such as $[Cu(CN)_4^{2-}]$ (Barakat, 2004), $[Fe(CN)_6^{3-}]$ (van Grieken et al., 2005), $[Zn(CN)_4^{2-}]$, and $[Cu(CN)_3^{2-}]$ (Ozcan et al., 2012).
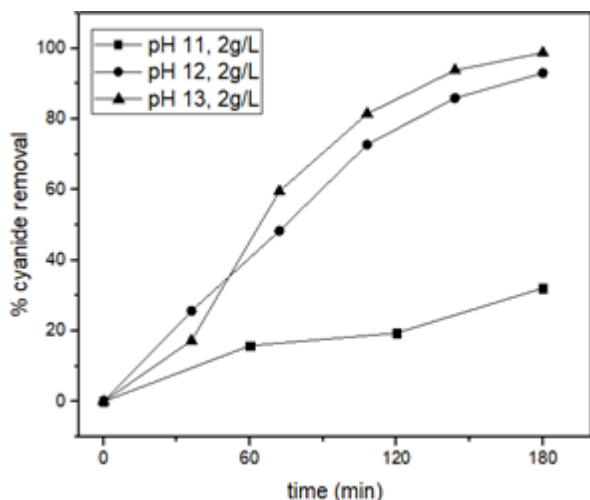

Figure 3 Removal of cyanide vs. time at various pHs at a TiO₂ concentration of 2 g/L
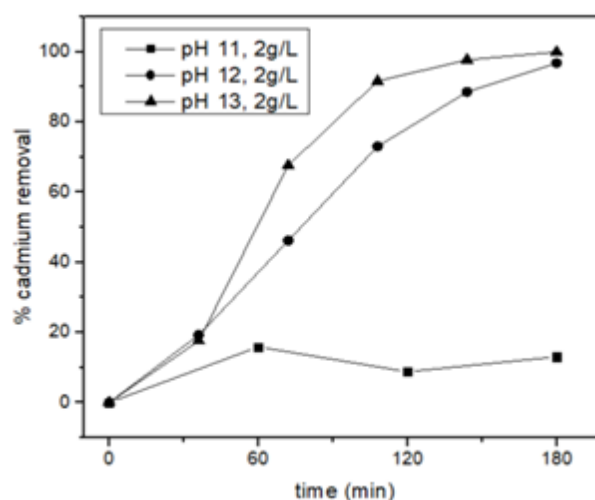
Figure 4 Removal of cadmium vs. time at various pHs at a TiO₂ concentration of 2 g/L

In the basic condition, although the free cyanide adsorption became much more difficult due to the TiO₂ surface becoming more negatively charged, the hydroxide ions could still react with the photogenerated holes in order to become hydroxyl radicals, which served as very potent oxidators for oxidizing the cyanide (Ozcan et al., 2012). This process can be expressed as follows.

$$CN^- + 2OH\bullet \rightarrow OCN^- + H_2O \tag{12}$$
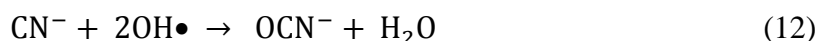
Moreover, the cadmium ion adsorption on the anatase should increase as the basic condition increases (Gao et al., 2004). When the cadmium was reduced, the cyanide would be released and then subsequently oxidized. Reduced cadmium was then deposited on the catalyst's surface so that the catalyst could be slowly deactivated at a later point (Chen & Ray, 2001). The cadmium cyano complex reduction should be similar to the $[Au(CN)_4^{2-}]$ and $[Ag(CN)_2^-]$ reductions (Litter, 1999; Munoz et al., 2009).

The contour plots (generated using Origin software) of the pseudo first-order rate constants of cyanide oxidation and cadmium reduction are shown in Figures 5 and 6, respectively. It was clearly shown that both the pH and the TiO$_2$ photocatalyst concentration played very important roles in the effectiveness of the wastewater treatment by UV/TiO$_2$ photocatalysis. At a low TiO$_2$ concentration, the reaction was quite slow, as reflected in its rate constant, due to the insufficient catalytically active surface area. The addition of a catalyst should initially improve both the oxidation and reduction rate up to a certain point. This improvement manifests because the increase in the catalytically active area results in more holes and electrons being generated due to the better absorption of UV light.

In most cases, when there is an excessive concentration of catalyst particles, the oxidation and reduction rates decrease due to the increase of reflected UV light on the catalyst surface, as well as the shielding effect that causes the UV light to barely penetrate the milky solution and be absorbed onto the photocatalytic surface (Papadam et al., 2007). However, it should be noted that there would be an interaction between the TiO$_2$ concentration and pH on the removal rate, since at a pH of approximately 12 and below the TiO$_2$ concentration had very little effect on the removal of Cd^{2+}, which showed that the pH played a dominant role due to the strong surface-adsorbate interaction. Another indication of the interaction between the TiO$_2$ concentration and the pH was illustrated by the effect of the pH on the cyanide removal rate at a low TiO$_2$ concentration, which obviously followed a very different pattern from that seen at a high TiO$_2$ concentration.
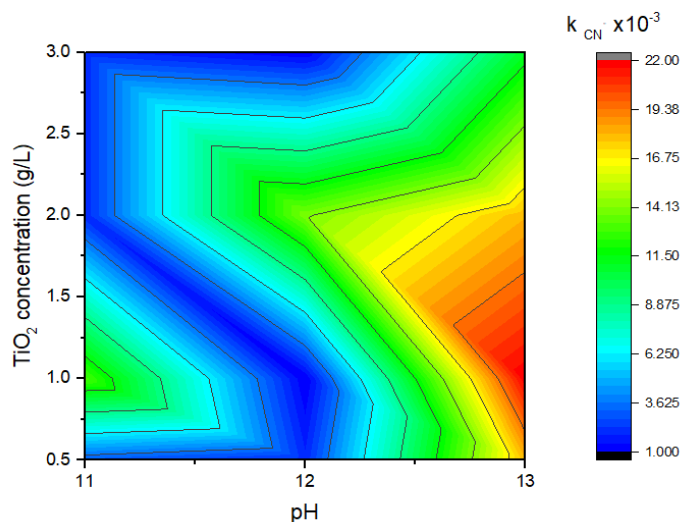

Figure 5 Pseudo first-order rate constant for cyanide oxidation at various pHs and TiO$_2$ concentrations
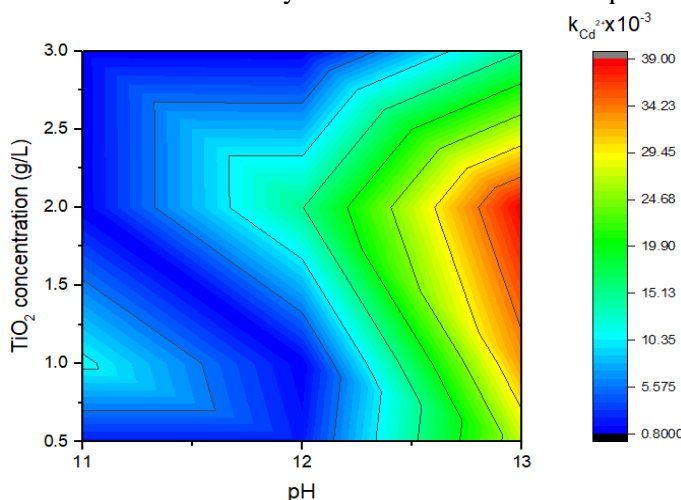

Figure 6 Pseudo first-order rate constant for cadmium reduction at various pHs and TiO$_2$ concentrations

The optimum conditions for wastewater treatment could be assessed using the pseudo first-order rate constants. For cyanide, the optimum condition was found at pH of 13 and a TiO_2 concentration of 1 g/L. The optimum condition for cadmium was slightly different, involving a pH of 13 but a TiO_2 concentration of 2 g/L. When the optimum conditions were applied, the removal rates for both cadmium and cyanide were higher than 95%, which was still higher than the Indonesian government's mandated threshold concentrations for both species in wastewater. In order to achieve an almost negligible concentration, another 120 minutes of treatment was needed for cyanide oxidation, while 90 minutes was needed for cadmium reduction.

4. CONCLUSION

Cadmium-cyanide wastewater treatment using UV/TiO_2 photocatalysis with an intensity of approximately 20 Watt/L could remove more than 95% of pollutants when at its optimum condition. The aeration rate, initial pH, and initial TiO_2 concentration were the major factors found to affect the reaction rate. For cadmium plating wastewater, it could be concluded that the optimum condition involves an initial pH of 13 and a TiO_2 concentration of around 1–2 g/L.

5. ACKNOWLEDGEMENT

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