Kinetics and Mass Transfer of Fixed Bed Photoreactor using N-Doped TiO$_2$ Thin Film for Tannery Wastewater under Visible Light

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A fixed bed photocatalytic reactor with N-doped TiO$_2$ thin film coated on stainless steel plate was conducted for tannery wastewater treatment under visible light irradiation. The photocatalytic efficiency was evaluated on a basis of changes on concentration of total chromium (Cr) and total organic carbon (TOC). Kinetics and mass transfer were determined from change of flow rate and the hydraulic retention time of wastewater in photoreactor. The photocatalytic reduction of total Cr followed pseudo-first order model with variation of feed concentration. The optimum flow rate in total Cr removal was found at 750 mL·min^{-1} with 1.20 mg·L^{-1}·min^{-1} initial reaction rate and 0.0452 min^{-1} kinetic rate constant. With the high flow rate (>750 mL·min^{-1}); both overall rate constant and photocatalytic efficiency was decreased. In the testing of photostability of the N-doped TiO$_2$ thin film in fixed bed photoreactor, the slight decrease of photocatalytic activity in total Cr and TOC removal after 6 cycles of tannery wastewater treatment was in an acceptable range which suggested that the photocatalyst can be successfully reused in wastewater applications.

1. Introduction

A fixed bed photocatalytic reactor incorporating TiO$_2$ catalyst and UV radiation was widely investigated for its performance in photocatalytic destruction of organic contaminants in fixed bed reactors (Nogueira and Jardim, 1996) and thin film variation (Noorjahan et al., 2003). Many researches have been conducted to increase its efficiency by introducing the combination of photocatalysis and solar technology to achieve the mineralization of pollutants presented in water at low cost – e.g. focusing on development (Bahnemann, 2004) as well as pilot plants (Malato et al., 2002). It is known that TiO$_2$ can use less than 5 % on the solar spectrum for photocatalytic oxidation (Romero et al., 1999) and the use of high energy UV light is not only costly but harmful as well (Muruganandham and Swaminathan, 2004). Recently, thin-film fixed bed reactor has been reported as one of the most popular solar photoreactor that can employ both direct and diffuse portions of solar irradiation at a light source and do not require the separation of the photocatalyst – pilot scale (Feitz et al., 2000) and commercial (Zayani et al., 2009). Another approach to increase photoreactor efficiency in utilize solar energy is to modify the catalyst to be effective under visible light. Many attempts have been made to make TiO$_2$ highly reactive, to allow utilization of the solar spectrum – e.g. (Ananpattarachai et al., 2009) focusing on light absorption ability, (Asahi et al., 2001) focusing on the catalysis), (Collazzo et al., 2012) on dye removal, (Fu et al., 2013) on the catalyst preparation. Although the high efficiency of N-doped TiO$_2$ in degradation of organic pollutants has been known, only a few publications demonstrated how effective of the visible light photocatalyst in wastewater application as a part of photocatalytic reactor (Hsu et al., 2011; Wu et al., 2013). To enhance the practicability in applying N-doped TiO$_2$ thin film to the environmental application, more research works in this area must be conducted.

This present study reports on our continuing work in using fixed bed photoreactor for contaminant removal (Kajivichyanukul et al., 2012). The tannery wastewater containing both chromium (Cr) and organic

contaminants was investigated using the fixed bed photocatalytic reactor and the N-doped TiO_2 thin films were used as immobilized catalyst. Kinetics and mass transfer of contaminants in the photocatalytic reaction under visible light were determined and reported.

2. Materials and methods

2.1 Materials

Chromium wastewater was received from a tanning industry, Thailand. This wastewater is collected prior to entering biological wastewater treatment. The wastewater had been filtrated prior to use in the photocatalytic processes described here. All reagents used in this research were analytical grade. Nanocrystalline titanium dioxide was prepared via sol-gel hydrolysis and condensation of ethanol solutions (Merck Chemicals) of titanium(IV) tetraisopropoxide (Sigma-Aldrich chemicals). Acetyl acetone was purchased from Carlo Erba chemical. The pH of the solution was adjusted to the desired value by adding NaOH or H_2SO_4, both of which were prepared by Merck Company, and used as received.

2.2 Methods

The synthesis of N-doped TiO_2 and the dip-coating of stainless steel plates to obtain the N-doped thin film TiO_2 to be used in fixed bed photoreactor were performed as previously described (Ananpattarachai et al., 2009). In brief, a modified sol–gel method was used to synthesize N-doped TiO_2 with a mole ratio of 1:20:1:1:1 for TTiP:EtOH:HNO_3:H_2O:Diethanolamine. First, TTiP was dissolved in EtOH and stirred for 30 min. In a second solution, EtOH was mixed with H_2O containing HNO_3 and stirred to promote hydrolysis until transparent. After mixing both portions, precipitation readily occurred. The dopant was then added to the solution. After obtaining the homogeneous transparent solution, the stainless steel plates were dipped into the solution and withdrawn at a constant speed to make a gel coating film. The TiO_2 gel films on stainless steel plates were heated at 800 °C in an electric furnace in a N_2 atmosphere. The samples were held at the peak temperature for 30 min before cooling to room temperature. The dip-drying procedure was repeated for 6 cycles. Selected coated stainless steel plates were cut into several 1 cm^2 pieces and gold-coated by using a sputter coater for determination of thickness and surface roughness of the TiO_2 film by a scanning electron microscope (SEM) (LEO1455VP).

The experimental assembly of the fixed bed photocatalytic reactor was conducted as previously described (Kajivichyanukul et al., 2012). The reactor consisted of a light source, coated stainless steel plates, a reaction tank with baffle and a reservoir. The visible light source (Sylvania, 150 W halogen lamp, wavelength 420 nm) or UV light source (Purely UV, 150 W low pressure mercury arc lamp, wavelength 254 nm) was placed above the photoreactor. In this photoreactor, the tannery waste stream was stored in a reservoir and was continuously circulated in the system by a peristaltic pump with variable speed for flow rate control, and the temperature was maintained as 25 ± 2 ºC in nitrogen or oxygen atmosphere. The total volume of the wastewater in the system was 20 L. To reach equilibrium the liquid was allowed to circulate for 30 min in the dark before the reaction was started by switching on the lights. The influent feed stream was pumped into the reactor and then recycled through the reactor after mixing in the reservoir. The solution within the reservoir was well mixed by magnetic stirring. The effluent from the reactor was mixed with the feed solution in the reservoir and recirculated through the reactor. Thus the overall operation was in the continuous recycle mode with multiple passes through the reactor. The effluent from photoreactor was submitted to routine wastewater analysis. Total chromium concentration was measured by atomic adsorption spectroscopy (Hitachi Z-2000). Total organic carbon (TOC) was measured using a TOC Analyser (Shimadzu TOC-L). Residual TiO_2 downstream of the reactor was also measured by atomic adsorption spectroscopy. No catalyst was observed to strip off the plates under the experimental conditions.

3. Results and discussion

Characteristics of TiO_2 thin film

Thin films of N-doped TiO_2 prepared by sol-gel process with dip-coating technique were analysed by SEM (LEO1455VP). The grain boundary of stainless steel was clearly seen. The coating cycles in dip-drying procedure at 6 coating cycles is shown in Figure 1, which indicates that the thickness of TiO_2 layer was uniform and smooth surface on stainless steel plate. From X-ray Diffraction analysis, all titania catalysts used in this study were anatase crystal phase as shown in Figure 2.

3.1 Characteristics of tanning wastewater

To evaluate the analytical characteristics and the biological treatability, total Cr and TOC values were carried out in triplicate from the mixed wastewater. Initial concentration of total Cr was 35 mg·L^{-1} which was a mixture of hexavalent and trivalent chromium. Total organic carbon was relatively high concentration as

of 715 mg·L^{-1} which came from several types of organic chemicals in tanning process including formic acid, oxalate acid, etc. Approximately 90% of TOC were dissolved organic carbon (DOC).
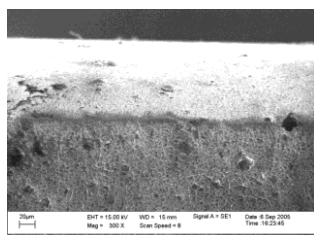

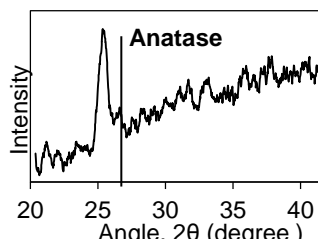Figure 1: SEM image of N-doped TiO$_2$ layer on stainless steel plate with 6 coating cycles

Figure 2: X-Ray diffraction pattern of N-doped TiO2 coating film deposited on stainless steel with 6 coating cycles

3.2 Comparison of photocatalytic activity of anatase TiO$_2$ and N-doped TiO$_2$ thin film under visible light

In this part, we used anatase TiO$_2$ and N-doped TiO$_2$ thin films as catalysts in identical fixed bed photoreactor with 750 mL.min^{-1} influent flow rate. The experiments were conducted in acidic pH (pH 3) for 2 h with bubbling air under visible light. Plots of removal efficiency for reduction of total Cr using N-doped TiO$_2$ and anatase TiO$_2$ under visible light in fixed bed photoreactor is shown in Figure 3.

Results show that the photocatalytic activity of N-doped TiO$_2$ under visible light was drastically improved relative to that of anatase TiO$_2$ under the same light condition. The improved efficiency of N-doped TiO$_2$ under visible light can be explained by a reduced energy requirement for N-doped TiO$_2$ owing to a decrease in band gap and a shift of absorption band. The suppression of electron-hole pair recombination owing to the new band structures created by nitrogen inclusion in N-doped TiO$_2$ was also the reason of this photocatalytic activity enhancement (Hsu et al., 2011).

3.3 Effect of feed flow rate on kinetic of fixed bed photoreactor under visible light

To study the effect of feed flow rate of waste stream on the kinetics of the fixed bed photoreactor, all experiments were conducted at a variable feed flow rate ranging from 100 to 1,000 mL·min^{-1}. Results of photocatalytic reduction of total Cr in different feed flow rates of tannery wastewater are shown in Figure 4a and 4b.
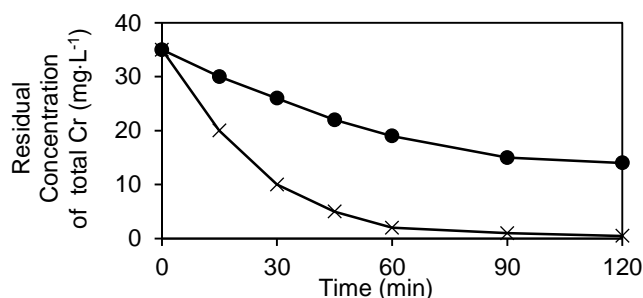

Figure 3: Comparison of removal efficiency of total Cr between anatase TiO$_2$ and N-doped TiO$_2$ in fixed bed photoreactor under visible light (-•-Anatase and -×-N-doped TiO$_2$)

To calculate the reaction kinetics of photocatalytic reactions obtained from different flow rates, the reaction can be well explained by a pseudo-first-order pattern, with the following equation demonstrating the relationship of *C* and *t*:

$$\ln\left[\frac{dC}{dt}\right] = kt \tag{1}$$

where *C* was the aqueous concentration of total Cr near the surface of the TiO$_2$ coating (mg·L^{-1}). The value of *k* was determined from the slope of the graph plotted between $\ln(C/C_0)$ and the reaction time. The R^2 value for linear regression was calculated to exhibit the tendency of the reaction, which followed the pseudo-first-order pattern. Values of initial rate, *r*, kinetic constant, k_{obs}, and the half-life of total Cr, $t_{1/2}$, calculated from the pseudo-first-order equations are shown in Table 1.
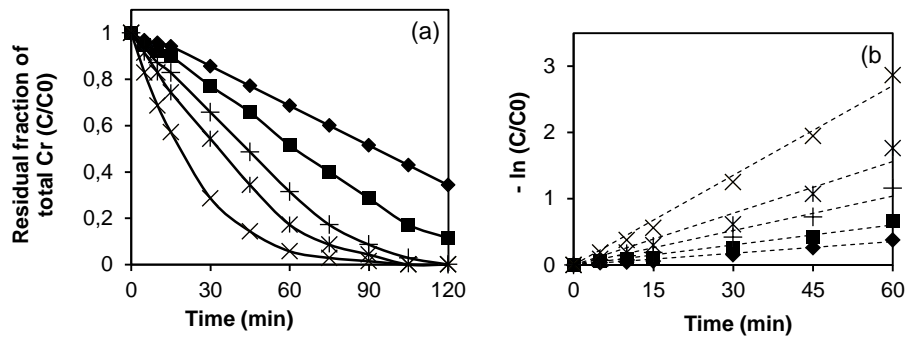
Figure 4: Results of photocatalytic reduction of total Cr: (a) the residual fraction plot and (b) the −ln(C/C₀) versus reaction time for total Cr removal in different feed flow rates; total Cr concentration 35 mg·L⁻¹; TOC concentration 715 mg·L⁻¹; pH 3 (-♦-100 mLmin⁻¹ -■-250 mLmin⁻¹ -✲-500 mLmin⁻¹ -✕-750 mLmin⁻¹ and -+-1,000 mLmin⁻¹)

*Table 1: Values of kinetic parameters including initial rate, **r**, kinetic constant, **k**ₒᵦₛ and half-life of total Cr, **t**₁/₂, based on feed flow rate of fixed bed photoreactor under visible light*

Flow rate (mL·min⁻¹)	Initial rate, r (mg·L⁻¹·min⁻¹)	Kinetic rate constant, k (min⁻¹)	Half-life, (min)	$t_{1/2}$R²
100	0.2170	0.0059	117.48257	0.9812
250	0.3520	0.0101	68.6284	0.9741
500	0.6000	0.0261	26.5574	0.9611
750	1.2000	0.0452	15.3351	0.9907
1,000	0.4400	0.0173	40.0663	0.9679

The efficiency as measured by the degradation of total Cr was best when the flow rate was adjusted to 750 mL·min⁻¹. The photocatalytic experiments using different flow rates showed variation in the reaction rate constants, k. within 2 h of visible light irradiation in the presence of the N-doped TiO₂ catalyst, the initial photocatalytic reaction rate of total Cr was 0.22, 0.35, 0.60, 1.20 and 0.44 mg·L⁻¹·min⁻¹ for feed flow rate as of 100, 250, 500, 750, and 1,000 mL·min⁻¹ respectively. This pattern suggests that the reaction rate can be enhanced by increasing of feed flow rate entering the fixed bed reactor. However, after peaking at 1.20 mg·L⁻¹·min⁻¹, both initial rate and kinetic rate constant were decreased with increasing feed flow rate, which was likely dependent on mass transfer during reaction.

Effect of feed flow rate on mass transfer of fixed bed photoreactor under visible light

Mass transfer consideration in a fixed bed photoreactor, can be divided into internal and external mass transfer. The internal mass transfer process is an intrinsic property of the catalyst film and is determined by the nature of the catalyst, coating porosity and the thickness of the catalyst film (Lin and Valsaraj, 2005). If the catalyst film is very thin, the internal mass transfer is negligible. External mass transfer occurs during the diffusion of contaminants from bulk liquid to reach the liquid-catalyst interface. In general, if the rate is influenced by the mass transfer term, then the apparent rate constant should increase with flow velocity or flow rate. As shown in Table 1, the rate constant was governed by flow velocity and peaked (0.0452 min⁻¹) at a waste stream flow rate of 750 mL·min⁻¹. The increasing of flow velocity also affected hydraulic retention time (HRT) defined as the time (t) that water remains in the photocatalytic reactor which can be calculated as follows:

$$HRT = \frac{V_{reactor}}{Q} \tag{2}$$

where V was the volume of reactor (L) and Q was the flow rate (L·min⁻¹). The relation among three parameters, flow rate, hydraulic retention time and rate constant is shown in Figure 5.

Results showed that the increasing of flow rate enhanced the turbulence, represented by the decreasing of hydraulic retention time (Figure 5), thus overcoming the limitation of mass transfer for fixed bed photoreactors. However, it can be seen that further increase of the flow rate (above 750 mL·min⁻¹) reduced the photocatalytic removal of total Cr. This decreasing in efficiency at higher flow rates has been observed for many types of photoreactors (Lin and Valsaraj, 2005; Zayani et al., 2009). Lin and Valsaraj (2005) stated that increasing the flow velocity over the immobilized catalyst causes a reduction in external mass transfer and tentatively decreases boundary layer resistance in the liquid phase, increasing of the overall rate constant (as we can see from this work). The decrease in the reduction of total Cr at high flow rate may arise from limitation of visible light penetration on account of the rise of the liquid thickness and the

reduction of the hydraulic retention time which led to reduced surface reactions efficiencies (Zayani et al., 2009).

3.4 Photostability of N-doped TiO₂ nano-thinfilm

Photostability is a very crucial property of materials in photocatalytic reaction. Many studies have reported the photocatalyst deactivation of materials developed for use in photochemistry processes (Cho et al., 2001; Wu et al., 2013). The photostability of the N-doped TiO_2 under visible light was compared with anatase-TiO_2 under UV light as the reference. When the photocatalytic reactions were carried out in solution with 35 mg·L^{-1} total Cr and 715 mg·L^{-1} TOC with 750 mL·min^{-1} feed flow rate at pH 3 for 2 h irradiation. Results for total Cr removal and TOC degradation percentages in six subsequent cycles are reported in Figure 6.
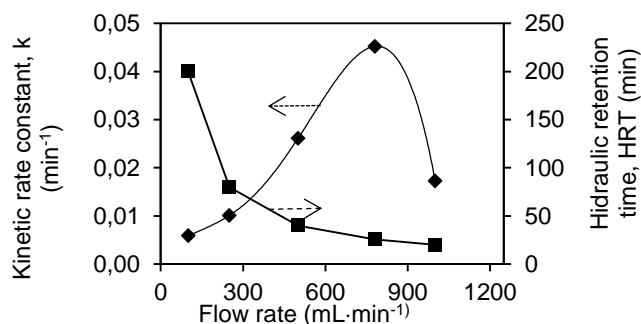

Figure 5: The kinetic rate constant and hydraulic retention time from different feed flow rate; total Cr concentration 35 mg·L^{-1}; TOC concentration 715 mg·L^{-1}; pH 3
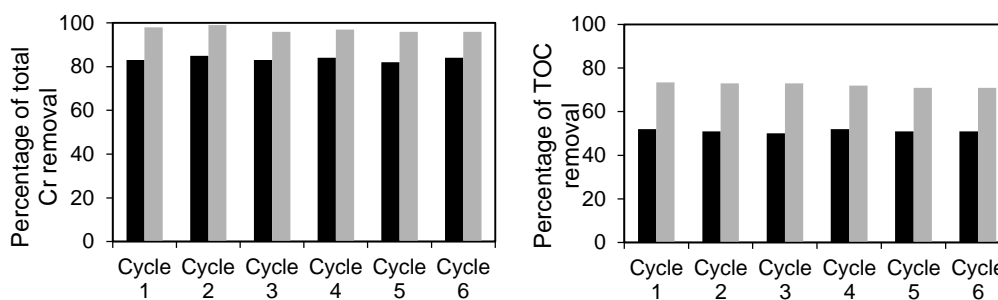

Figure 6: Photostability of N-doped TiO₂/visible and anatase TiO₂/UV during repeated cycles (a) percentage of total Cr removal and (b) percentage of TOC removal (■Anatase-TiO₂/UV and ■N-doped TiO₂/Visible)

Apparently, the efficiency of total Cr removal using N-doped TiO_2 under visible light was slightly decreased by 3 %, from 99 % to 96 %, and that of TOC degradation was decreased by 2 %, from 73 % to 71 %, during the running of 6 cycles of tannery wastewater. The high concentration of chloride ions in our tannery wastewater may contribute to the decreasing of photocatalytic activity as it was previously reported that a chloride concentration >4 g·L^{-1} can poison the catalyst (Cho et al., 2001). It is possible that the 3.8 g·L^{-1} of chloride ions identified in this study may be responsible to loss of activity. Nosaka et al. (2005) also reported the significant decrease of photocatalytic activity of N-doped TiO_2, which may be explained by the surface of the photocatalyst becoming covered with some by-products or the doped nitrogen atoms being released from the TiO_2 lattice. In addition, Gapen (1999) also reported that the high flow rate or velocities may cause the delamination of the TiO_2 film, which also leads to decreased reactor efficiency. However, the decrease of photocatalytic activity of the N-doped TiO_2 was in an acceptable range and could be reused to obtain high efficiencies of total Cr and TOC removal.

4. Conclusion

Photocatalytic activity of total Cr and TOC removal from tannery wastewater using fixed bed photocatalytic reactor was conducted in this work. This paper reported the innovative aspect in using N-doped thin film titania as catalyst under visible light irradiation in fixed bed photocatalytic process for industrial wastewater. Results from this work provided essential information needed towards the construction and operation of a fixed bed photocatalytic reactor. Specifically, we have evaluated: (a) the improvement of

photocatalytic activity using N-doped TiO_2 for both total Cr and TOC removal; (b) kinetic and mass transfer characteristics in a fixed bed photoreactor; and (c) photostability of N-doped TiO_2 thin film in fixed bed photoreactor.It was found that the photocatalytic reduction reaction follows the pseudo-first order model with variation of feed concentration. The increasing of flow rate enhances the turbulence to overcome the limitation of mass transfer for fixed bed photoreactor. The optimum flow rate was found at 750 mL·min^{-1}. With the very high flow rate (>750 mL·min^{-1}); the decreasing both of overall rate constant and photocatalytic efficiency was seen owing to the delamination of the TiO_2 film. Finally, photocatalytic efficiencies in total Cr and TOC removals using N-doped TiO_2 thin film under visible light was slightly decreased with an increasing of cycle times. The high concentration of chloride ions in our tannery wastewater may contribute to the decreasing of photocatalytic activity. However, the decrease of photocatalytic activity of the N-doped TiO_2 after 6 cycles of tannery wastewater treatment was in an acceptable range and could be reused to obtain high efficiencies of total Cr and TOC removal.

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