

# Preparation of Titanium Dioxide (TiO<sub>2</sub>) from Sludge produced by Titanium Tetrachloride (TiCl<sub>4</sub>) Flocculation of Wastewater

H.K. Shon<sup>1\*</sup>, S. Vigneswaran<sup>1</sup>, In S. Kim<sup>2</sup>, J. Cho<sup>2</sup>

G.J. Kim<sup>3</sup>, J.B. Kim<sup>4</sup>, J.-H. Kim<sup>4,5</sup>

<sup>1</sup> Faculty of Engineering, University of Technology, Sydney, P.O. Box 123, Broadway, NSW 2007, Australia

<sup>2</sup> Department of Environmental Science and Technology, Gwangju Institute of Science and Technology, Gwangju, Korea

<sup>3</sup> Department of Chemical Engineering, 253 Yonghyun-dong, Nam-gu, Inha University, Incheon, 402-751, Korea

<sup>4</sup> Photo & Environmental Technology Co. Ltd., Gwangju 500-460, Korea

<sup>5</sup> School of Applied Chemical Engineering & The Institute for Catalysis Research, Chonnam National University, Gwangju 500-757, Korea, Chonnam National University, Gwangju 500-757, Korea

\* The author to whom all the correspondence should be addressed (Tel.: 61295142629, Fax: 61295142633). Email: hkshon@eng.uts.edu.au

## Abstract

Sludge disposal is one of the most costly and environmentally problematic challenges of modern wastewater treatment worldwide. In this study, a new process was developed, which has a significant potential to the lower cost of waste disposal, protect the environment and public health and yield economically useful by-products. Titanium oxide (TiO<sub>2</sub>) which is the most widely used metal oxide was produced from the wastewater sludge generated by the flocculation of secondary wastewater with titanium tetrachloride (TiCl<sub>4</sub>). Detailed analyses were conducted to compare TiCl<sub>4</sub>, ferric chloride (FeCl<sub>3</sub>) and aluminum sulfate (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>) flocculation. Removal of organic matter and different molecular sizes by Ti-salt flocculation was similar to that of the most widely-used Fe- and Al-salt flocculation. The mean size of Ti-, Fe- and Al-salt flocs was 47.5 μm, 42.5 μm and 16.9 μm, respectively. The decantability of the settled flocs by TiCl<sub>4</sub> coagulant was similar to that by FeCl<sub>3</sub> coagulant and much higher than that of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. The photocatalyst from wastewater (PFW) produced by TiCl<sub>4</sub> flocculation was characterized by X-ray diffraction (XRD), BET surface area, scanning electron microscopy/energy dispersive X-ray (SEM/EDX), transmission electron microscopy (TEM), photocatalytic activity and X-ray photoelectron spectroscopy (XPS). The resulting PFW was found to be superior to commercial TiO<sub>2</sub> (P-25) in terms of photocatalytic activity and surface area. The PFW was also found to be mainly doped with C- and P- atoms. The atomic percentage of the PFW was TiO<sub>1.42</sub>C<sub>0.44</sub>P<sub>0.14</sub>.

**Keywords:** flocculation, titanium oxide, waste prevention, wastewater

## **Introduction**

### **Problem of flocculation in treating wastewater**

Systematic treatment of wastewater for the prevention of pollution and disease in urban society commenced in the late 19<sup>th</sup> and early 20<sup>th</sup> centuries (1). For the last century, wastewater treatment has continually been refined to improve its performance and meet stringent disposal standards. These treatment processes use a range of physical, chemical and biological methods. Chemical treatment involves the removal or conversion of contaminants by the addition of particular chemicals or by other chemical reactions (2). Flocculation is one of the most common chemical treatment methods and causes contaminants to coagulate. Flocculation can also be used for removing organic matter, which causes trihalomethane formation during disinfection (3). Commonly-used coagulants include: i) aluminum sulfate (72%), ii) iron salts (23%), and iii) polyaluminum chlorides (5%) (4). The use of ferric chloride and polyaluminum chloride for water treatment has been increasing over the last few decades. However, the flocculation process using these coagulants produces large quantities of sludge which inhibit efficient wastewater treatment. Most of this sludge is solid waste from which nothing can be recovered or reused and which then requires further treatment such as incineration, landfill, etc. A coagulant that produces less sludge or more reusable sludge offers a novel solution to many environmental and economic problems associated with sludge handling.

### **Problems in preparing TiO<sub>2</sub>**

Titanium oxide (TiO<sub>2</sub>) is the most widely used metal oxide in environmental applications for degradation of waste. This proceeds via an oxidative (electrophilic) attack of HO• and leads to complete mineralization yielding CO<sub>2</sub> and mineral acids. This process is based on the electronic excitation of a molecule or solid caused by absorption of ultraviolet (UV) light that drastically alters its ability to lose or gain electrons and promotes the decomposition of pollutants into harmless by-products (5). Photoinduced electrons (e<sup>-</sup>) and positive holes (h<sup>+</sup>) are produced from TiO<sub>2</sub> with UV light. These charged species can further generate free radicals. The highly oxidizing positive hole (h<sup>+</sup>) is considered to be the dominant oxidizing species in the mineralization process resulting from the TiO<sub>2</sub> photocatalysis (6). The usefulness of TiO<sub>2</sub> for degrading contaminants in many applications means that demand for it is increasing greatly. Generally, TiO<sub>2</sub> is produced using methods such as: i) sulfate method, ii) chloride method (vapor method), iii) alkoxide method and iv) specific method (7). To activate the photocatalytic activity, i) cationic and anionic loading, ii) thermal treatment, and iii) hydrothermal treatment have been applied. Transitional metals (Fe, Ni, Cr, Co, W and V), metal oxides (Fe<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, CoO<sub>2</sub>, MgO + CaO and SiO<sub>2</sub>) and transitional ceramics (WO<sub>3</sub>, MoO<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub>, SnO<sub>2</sub> and ZnO) are often used to coat and dope TiO<sub>2</sub> to improve its effectiveness (8). However, the problem is that the processes used to produce TiO<sub>2</sub> still discharge a large amount of wastewater which contains strong acid

and chloride/sulfate ions at high concentrations.

This study aimed to solve three major environmental problems:

- i) removal of organic matter by flocculation from wastewater,
- ii) sludge reduction after flocculation and
- iii) TiO<sub>2</sub> production from wastewater

We used titanium salt (TiCl<sub>4</sub>) instead of iron (FeCl<sub>3</sub>) and aluminum (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>) salts as an alternative coagulant and investigated removal of organic matter. The molecular weight (MW) distribution of organic matter removed was also investigated in wastewater. After flocculation with titanium salt the settled floc was incinerated at different temperatures to produce TiO<sub>2</sub>. The TiO<sub>2</sub> produced was thus characterized by X-ray diffraction (XRD), Brunauer, Emmett and Teller (BET) surface area, scanning electron microscopy/energy dispersive X-ray (SEM/EDX), transmission electron microscopy (TEM), photocatalytic activity and X-ray photoelectron spectroscopy (XPS) to evaluate its quality.

## **Experimental**

### **Organic removal and MW distribution by flocculation**

Flocculation was carried out with different coagulants (TiCl<sub>4</sub>, FeCl<sub>3</sub>, and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>) with different doses in synthetic wastewater. The composition of the synthetic wastewater is presented in Table 1 (9-10). This synthetic wastewater represents effluent organic matter generally found in biologically-treated sewage effluent. Tannic acid, peptone, sodium lignin sulfonate, sodium lauryl sulfate and arabic acid represent the larger MW portion, while peptone, beef extract and humic acid comprise the organic matters of lower MW. The samples were stirred rapidly for 1 minute at 100 rpm, followed by 20 minutes of slow mixing at 30 rpm, and 30 minutes of settling. Organic matter was measured using a Dohrmann Phoenix 8000 UV-persulphate TOC analyzer equipped with an autosampler. All samples were filtered through 0.45 µm membrane prior to organic measurement. The synthetic wastewater was also examined for the MW distribution of organics by high pressure size exclusion chromatography (HPSEC, Shimadzu Corp., Japan) with a SEC column (Protein-pak 125, Waters Milford, USA). Standards of MW of various polystyrene sulfonates (PSS: 210, 1800, 4600, 8000, and 18000 daltons) were used to calibrate the equipment.

Table 1 Constituents of the synthetic wastewater used in this study

Compounds	Concentration (mg/L)	Molecular weight (daltons)	Fraction by organic matter
Beef extract	1.8	300, 100, 70	0.065
Peptone	2.7	34300, 100, 80	0.138
Humic acid	4.2	1500, 300	0.082
Tannic acid	4.2	6300	0.237
Sodium lignin sulfonate	2.4	12100	0.067
Sodium lauryl sulphate	0.94	34300	0.042
Arabic gum powder	4.7	900, 300	0.213
Arabic acid (polysaccharide)	5.0	38900	0.156
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	7.1		0
K <sub>2</sub> HPO <sub>4</sub>	7.0		0
NH <sub>4</sub> HCO <sub>3</sub>	19.8		0
MgSO <sub>4</sub> •7H <sub>2</sub> O	0.71		0

### Characterization of settled floc after flocculation

The floc size distribution was investigated with a laser particle size analyzer (LS-230, Beckman Coulter, USA). SETSYS Evolution TGA (SETARAM Instrumentation, Co. Ltd.) was used to measure the simultaneous thermogravimetric analysis (TGA) and differential thermal analysis (DTA).

### Characterization of TiO<sub>2</sub>

Zeta potential of TiO<sub>2</sub> produced by settled floc after incineration was determined by electrophoresis method (ELS 8000 Otsca, Japan) with 1 mM KCl electrolyte. XRD images (Rigaku, Japan) of anatase and rutile TiO<sub>2</sub> photocatalysts to identify the particle structure was investigated. All the XRD patterns were analyzed with MDI Jade 5.0 (Materials Data Inc., USA). The crystallite size and interplanar distance of powders were determined from the broadening of corresponding X-ray diffraction peaks by using Bragg's and Scherrer's formulas, respectively. UV-VIS-NIR spectrophotometer (Cary 500 Scan, Varian, USA) was used to identify the absorbance range and the band gap of TiO<sub>2</sub> was calculated. The photocatalytic activity test of TiO<sub>2</sub> was investigated under irradiation of UV (Sankyo, F10T8BLB, three 10 W lamps) and visible light (Kumbo, FL10D, three 10W lamps) using the method of photodecomposition of gaseous acetaldehyde. The concentration of acetaldehyde was measured by gas chromatography (Youngin, M600D, Korea). XPS measurements were performed with a Leybold LHS10 spectrometer, equipped with a twin anode (Mg K $\alpha$ /Al K $\alpha$ ) non-monochromatised source (operated at 280 W) and a hemispherical electron analyzer. The visual microscopy was used to measure the shape and size of TiO<sub>2</sub>. SEM and TEM (Rigaku, Japan) were measured. Micromeritics Gemini 2360 analyzer (USA) for BET surface area analysis was used with automatic surface area analyzer.

## Results and Discussion

### Comparison of $\text{TiCl}_4$ with $\text{FeCl}_3$ and $\text{Al}_2(\text{SO}_4)_3$ flocculation

In order to evaluate the relative merits of Ti-salt flocculation, we compared the removal and MW distribution of organic matter by Ti-salt flocculation with those by Fe- and Al-salt flocculation using synthetic wastewater. Figure 1 shows the removal of organic matter after flocculation using different coagulants. The concentration of the  $\text{TiCl}_4$  coagulants was varied from 2.70 to 14.04 Ti-mg/L. The removal of organic matter was about 70% at 9.79 Ti-mg/L (Figure 1A). This organic removal was similar to that achieved with Fe and Al salts (Figures 1B and 1C). MW distribution of organic matter removed by different coagulants (Figure 2) was also investigated. All three coagulants resulted in similar organic removal in terms of the various MW ranges. They removed practically all the large MW organic matter. Further, this flocculation also helped in removing some of the small MW compounds (860 - 1000 daltons). However, the smallest MW range of compounds around 250 daltons could not be removed by any of the coagulants.

Figure 3 presents the size distribution of the settled flocs after Ti-, Fe- and Al-salt flocculation. The mean size of Ti-, Fe- and Al-salt flocs was 47.5  $\mu\text{m}$ , 42.5  $\mu\text{m}$  and 16.9  $\mu\text{m}$ , respectively. The decantability of the settled flocs was similar for  $\text{TiCl}_4$ ,  $\text{FeCl}_3$  flocculant and much higher than with Al salt. The World Health Organization's (WHO) (II) environmental health guidelines call for a Ti concentration in drinking water supplies of 0.5 – 15  $\mu\text{g/L}$ . The results from the inductively coupled plasma mass spectrometer (ICP-MS) suggest that about 10  $\mu\text{g/L}$  of Ti salt remained in the supernatant after the  $\text{TiCl}_4$  flocculation. Ti is also found in human urine, lung, kidney and liver tissues at trace concentrations. Long-term toxicological studies have not found Ti salt in water to have any adverse effects. All the above factors suggest that the  $\text{TiCl}_4$  can be used as an alternative coagulant.

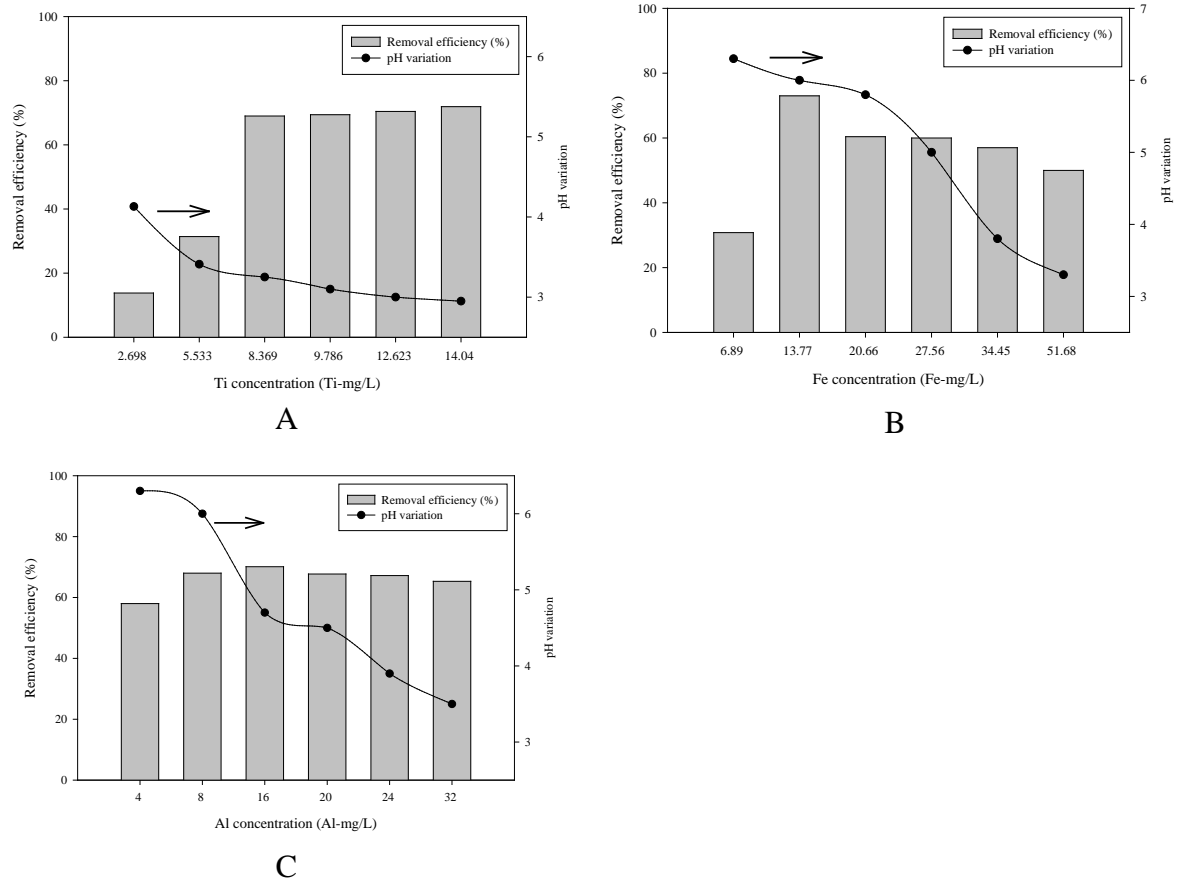


Fig. 1 Organic removal during A) Ti-salt flocculation, B) Fe-salt flocculation and C) Al-salt flocculation of wastewater (initial concentration of organic matter (in terms of total organic carbon) = 10.05 mg/L; initial pH = 7.3).

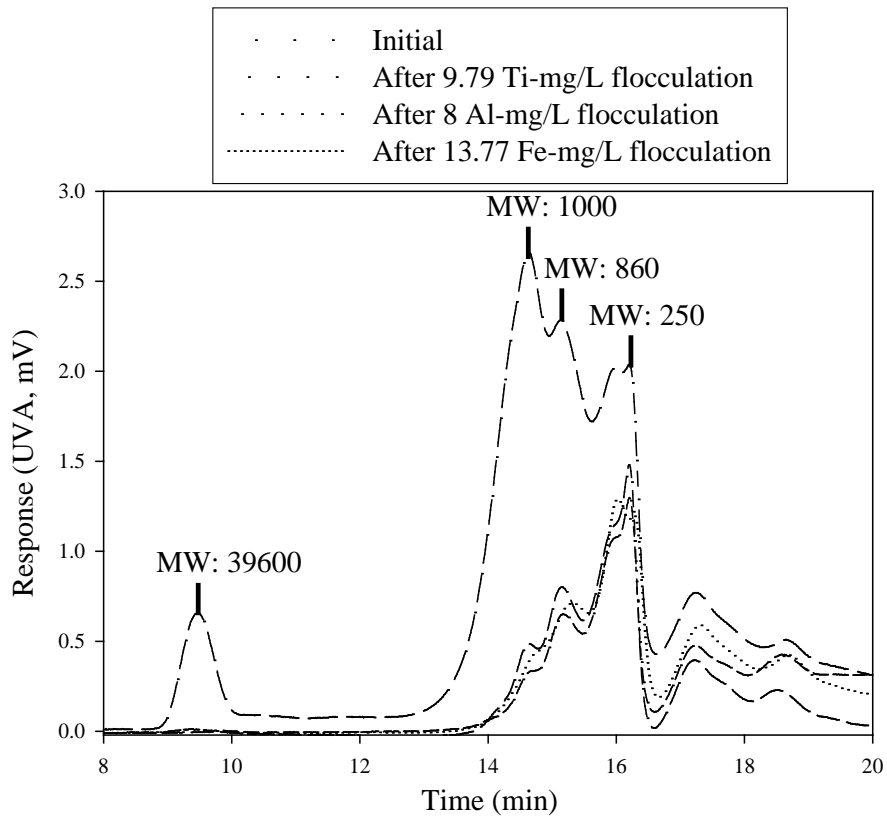


Figure 2 MW distribution of organic matter by different flocculations

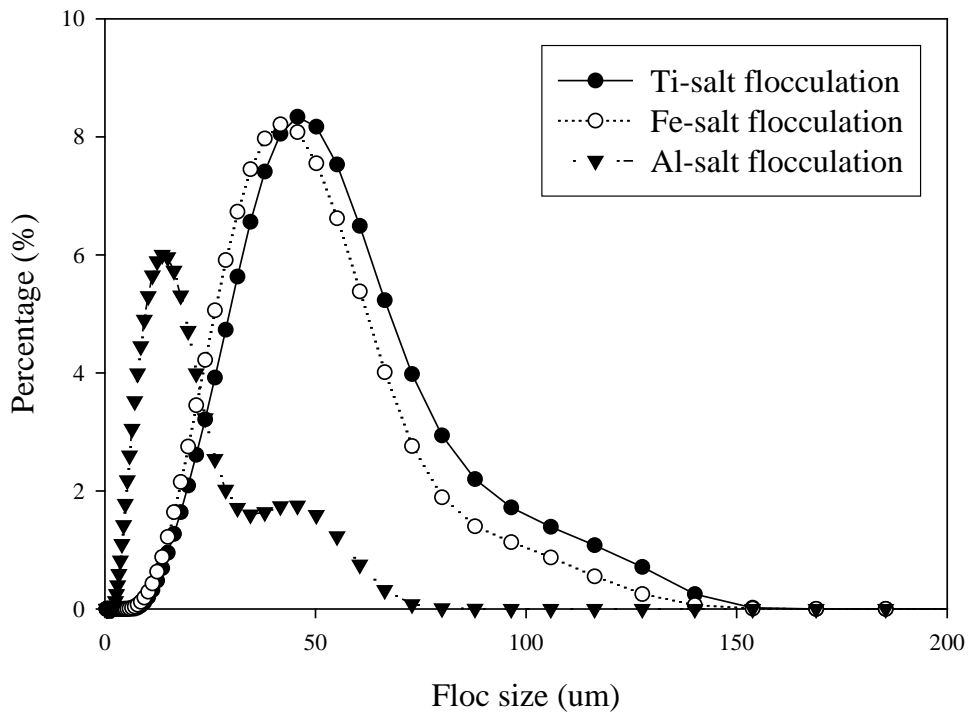


Figure 3 MW distribution of the settled flocs after different flocculations

## Preparation of the functional TiO<sub>2</sub>

In order to investigate the possibility of recycling the settled floc produced by Ti-salt flocculation, the settled floc at different temperatures between 100 °C and 1000 °C was incinerated. As the temperature increased, the color of the incinerated floc changed from black to white. The black color may be due to the remaining organic matter at lower temperatures. The thermogram recorded for the settled floc after Ti-salt flocculation is shown in Figure 4. The thermal treatment of floc up to 100°C led mainly to the loss of water content while between 100 to 450°C it resulted in removal of organic matter. The water content accounted for 55% and the organic matter 20% in the settled floc.

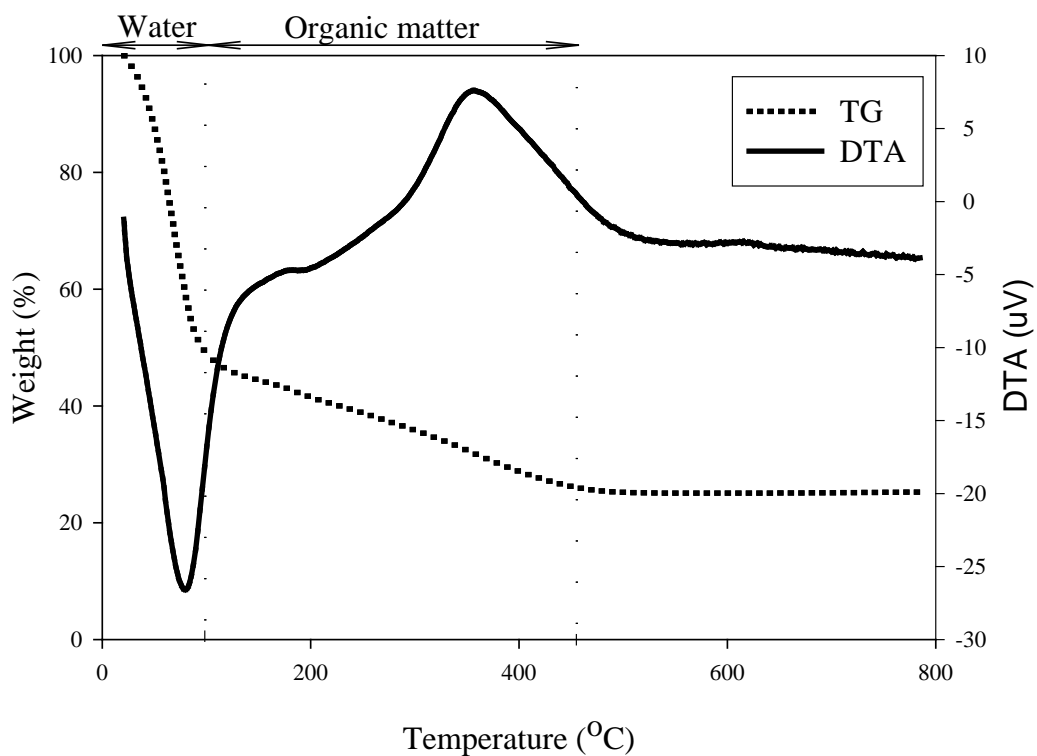


Figure 4 Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the settled floc after Ti-salt flocculation



XRD images were made to identify the particle structures of the settled floc after incineration at different temperatures (Figure 5). The anatase structure was observed at 600 °C and 800 °C and at 1000 °C, the anatase structure changed to rutile. However, below 600 °C, an amorphous structure was observed which may be due to the remaining organic matter at low temperatures. Although there were many different molecules in the wastewater sample, only TiO<sub>2</sub> structure was found after incineration above 600 °C. Here, the narrower XRD pattern of the annealed sample at 1000 °C was found to be comparable with that at 600 °C. This may be due to the grain growth at higher temperatures (12). Based on the results of Liao et al., (13), the transformed temperature of the anatase to rutile at ambient pressure was approximately 550 °C. However, in this study, this transformation occurred at above 800 °C. The impurity of the TiO<sub>2</sub> produced by the settled floc was about 20% with C and P atoms. This may be due to the impurity of the TiO<sub>2</sub>. However increased temperatures involve higher energy consumption and cost. Thus 600 °C was selected as the most effective temperature taking into account energy requirement and photocatalytic activity. The TiO<sub>2</sub> produced in this way is referred to hereafter as “photocatalyst from wastewater (PFW)”.

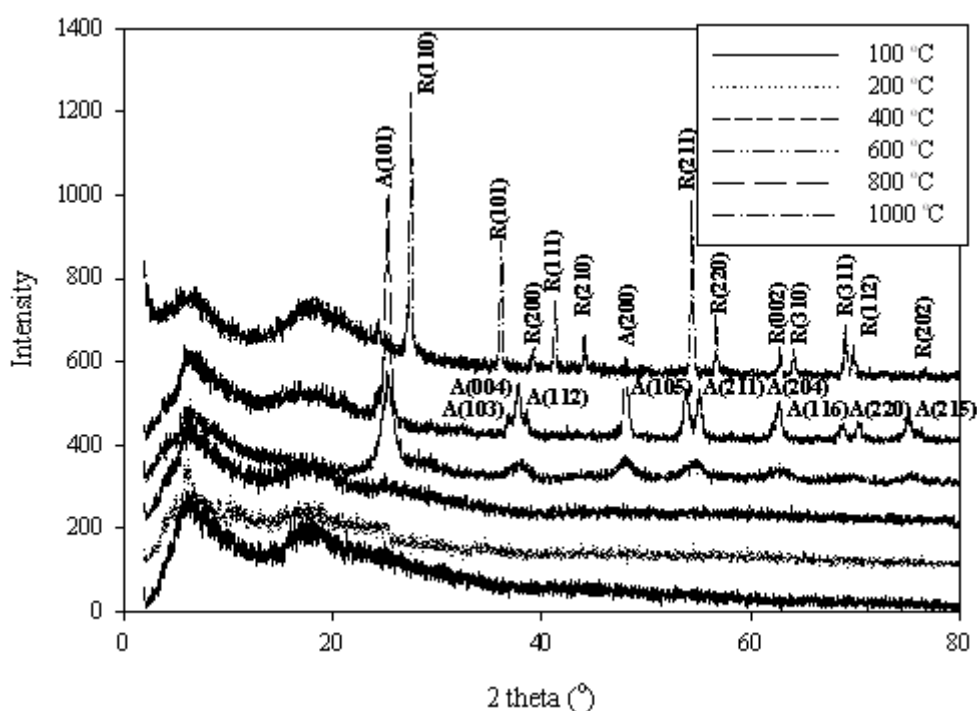


Figure 5 XRD image of the settled Ti-salt floc after incineration at different temperatures (A: anatase; R: rutile)

## Characteristic of the functional TiO<sub>2</sub>

The crystallite size of the PFW calculated by the Scherrer's formula (14) was 6.0 nm and it consisted of the anatase structures, based on high resolution TEM measurement (Figure 6). The BET specific surface area of the PFW was 76.3 m<sup>2</sup>/g, which was higher than that of the P-25 TiO<sub>2</sub>, the most widely used photocatalyst (15).

For the detailed investigation of a doping atom in the PFW, we measured SEM/EDX, TEM and XPS. Based on the SEM/EDX results, C and P atoms were found to be mainly doped in/on the PFW. The elements were uniformly spread in/on the PFW (Figure 7). The radial structure functions (RSFs) of Ti K-edge extended X-ray absorption fine structure (EXAFS) of the PFW were measured. The major peaks were found in the PFW corresponding to shells of O atoms (~0.13 nm), C/P atoms (~0.249 nm), Ti atoms (~0.27 nm), and a mixed shell of O and Ti atoms (~0.33 nm). To determine the composition of the PFW and identify the valence states of various atoms present, we carried out XPS analyses. The windows of the survey spectrum were recorded for each constituent (titanium, oxygen, carbon and phosphorus) in multi-scan recording mode (Figure 8). The titanium was mainly present in the form of Ti<sup>4+</sup>. Nocun (16) reported that a titanium atom of Ti<sup>4+</sup> depended on the melting conditions. High oxidation led to a higher Ti<sup>4+</sup> content. The binding energy of the Ti 2p<sub>3/2</sub> line was found at 458.96 eV (after the correction was made to the C 1s line in order to take into account the charge effects). The atomic percentage of Ti, O, C and P of the PFW was 26.9:51.5:15.8:5.8 or TiO<sub>1.42</sub>C<sub>0.44</sub>P<sub>0.14</sub>. That of Ti and O with P-25 photocatalyst was 23.0:76.0, respectively. This suggests that in PFW, most of the C and P atoms were doped as a substitute site for an O atom.

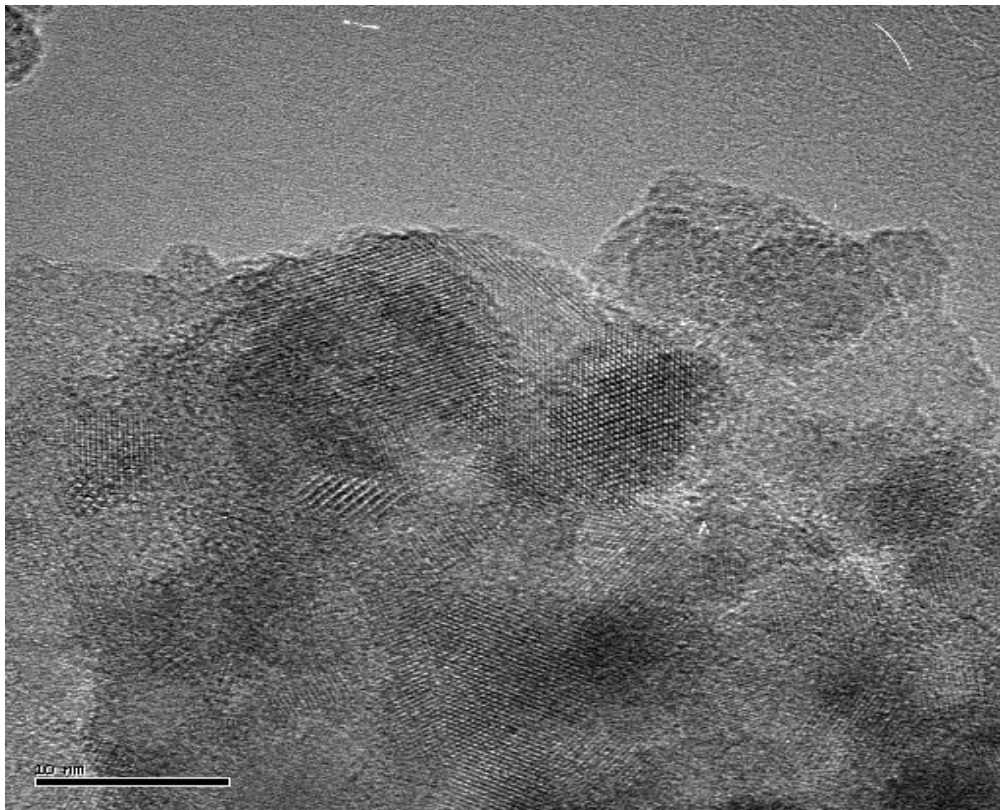


Figure 6 High resolution transmission electron microscope (HRTEM) image of the PFW

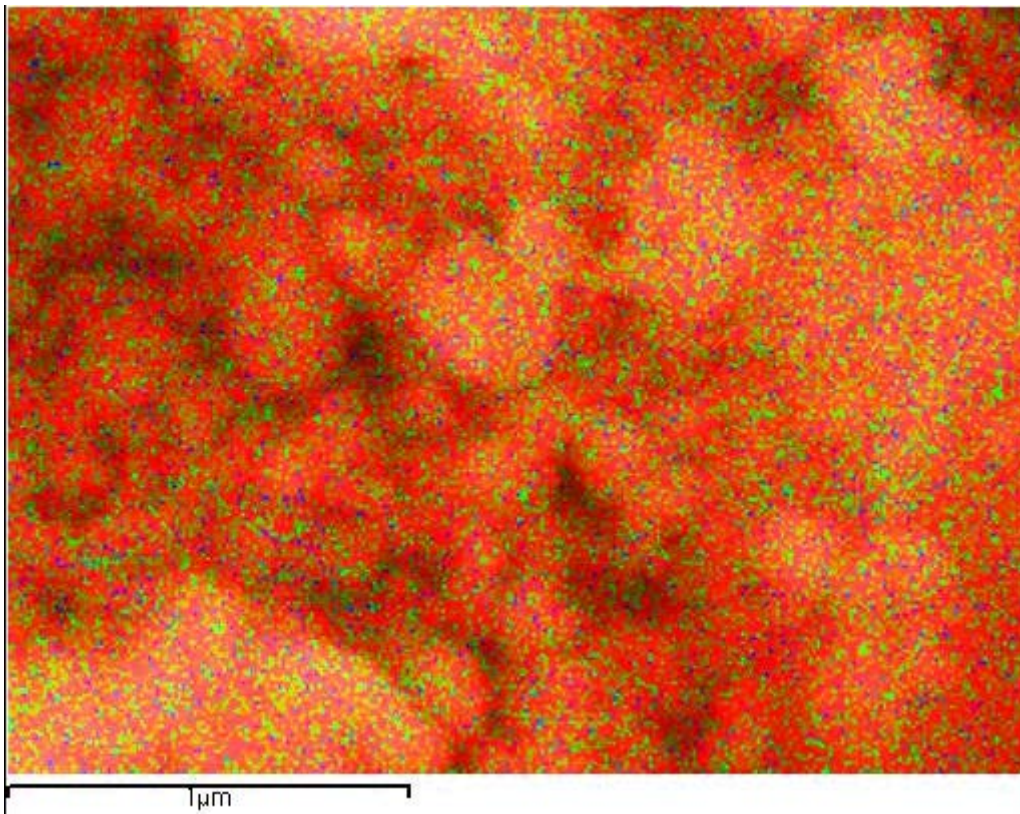


Figure 7 SEM/EDX element map of the PFW (Ti: red; C: green; P: blue)

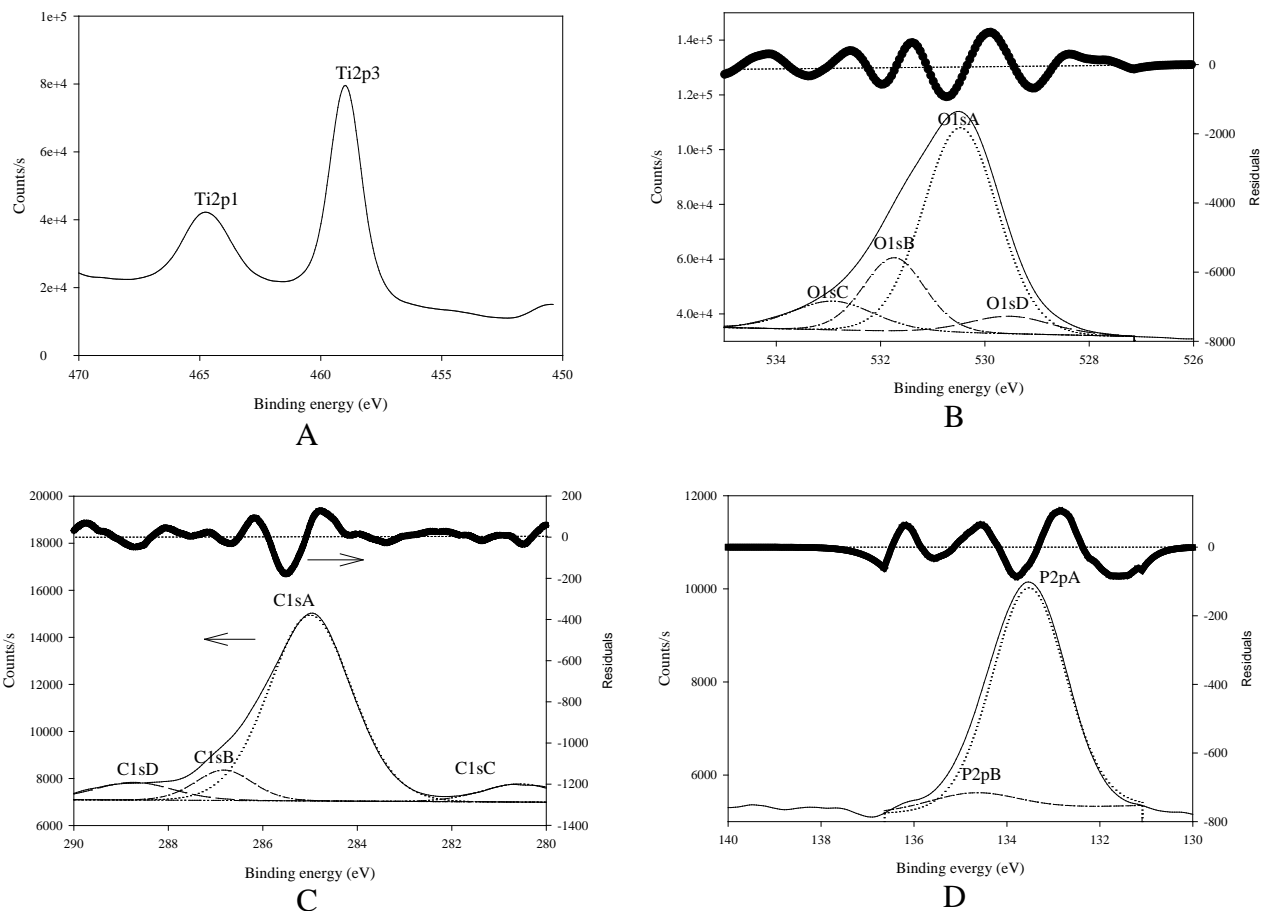


Figure 8 XPS spectrum of different elements in the PFW (A: Ti atom window; B: O atom; C: C atom; D: P atom)

A number of studies have focused on the development of visible-light photocatalysts (8, 17). These photocatalysts can be made by doping transitional metals and/or non-metals. The optical property of the PFW was thus investigated using the ultra violet–visible–near infrared (UV-VIS-NIR) spectrophotometer (Figure 9). The P-25 photocatalyst absorbed the majority of UV light (less than a 400 nm wavelength). The PFW photocatalyst however absorbed not only UV light but also visible light (407 nm and 3.05 eV).

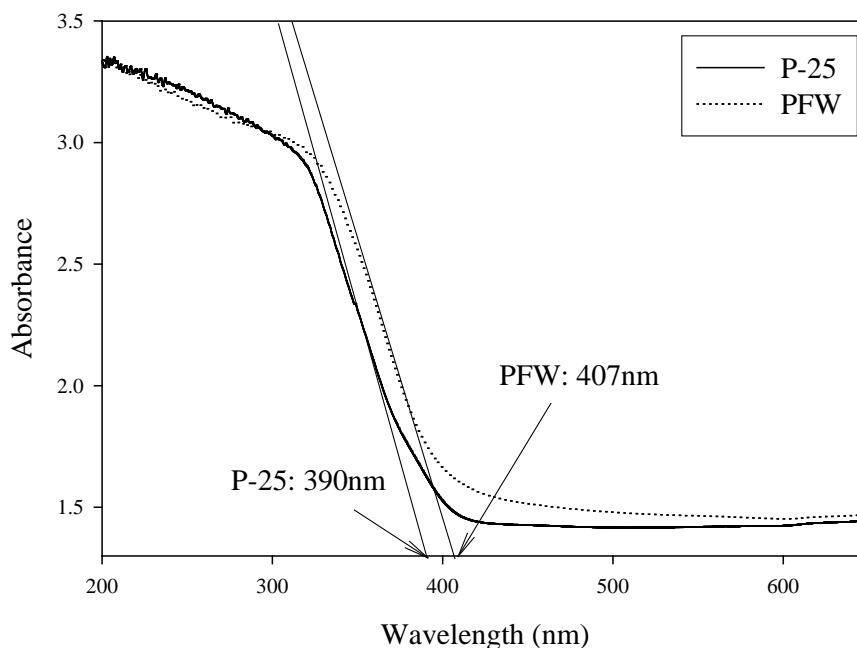


Figure 9 Optical absorbance of P-25 and PFW photocatalysts

### Removal of acetaldehyde by the functional TiO<sub>2</sub>

The photocatalytic property of the PFW was investigated under irradiation of UV and visible light for the photodecomposition of gaseous acetaldehyde (Figure 10). The concentration of acetaldehyde was measured by gas chromatography. The photodecomposition rate of acetaldehyde using the PFW was compared to that of the P-25 photocatalyst. Without any light sources, both the PFW and P-25 photocatalysts adsorbed acetaldehyde up to 18% in the first 15 minutes. The removal of acetaldehyde with the PFW was higher than that with the P-25 under UV irradiation. After 90 minute of photocatalytic reaction, the PFW photocatalysis removed the majority of acetaldehyde.

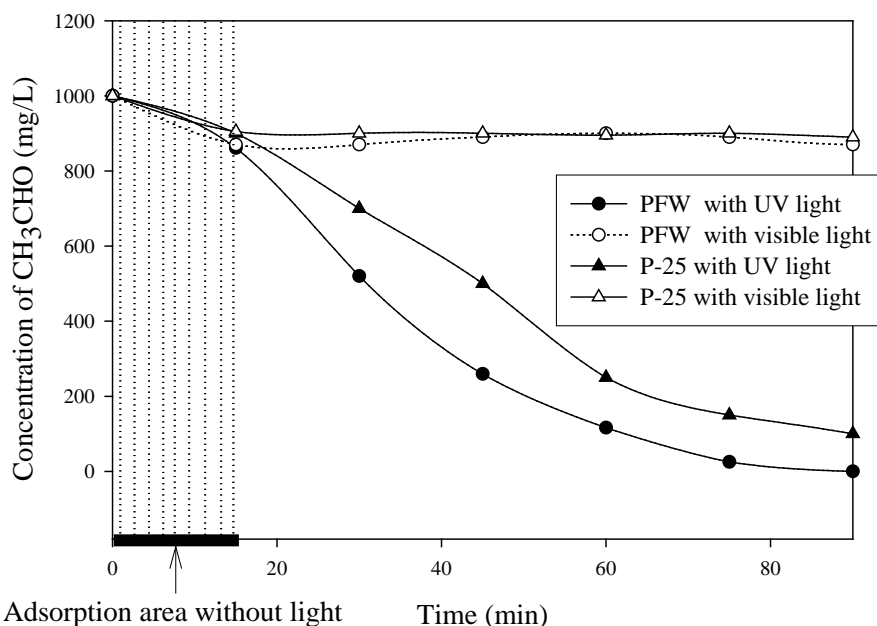


Figure 10 Variation of  $\text{CH}_3\text{CHO}$  concentration with irradiation time (initial concentration of  $\text{CH}_3\text{CHO} = 1000 \text{ mg/L}$ ; UV irradiation = black light three 10 W lamps; visible light irradiation = fluorescent light at 436 nm and a light power of  $0.9 \text{ mW/cm}^2$ )

In summary, the alternative coagulant ( $\text{TiCl}_4$ ) changes into  $\text{TiOCl}_2$  in wastewater. Depending on pH, the  $\text{TiOCl}_2$  hydrolyzes to  $\text{Ti}(\text{OH})_4$  (4). As the zeta potential of the negatively-charged organic matter is broken by  $\text{Ti}(\text{OH})_4$ , organic matter aggregates with the  $\text{Ti}(\text{OH})_4$  (5). Here phosphorus and a variety of metal compounds are found in the wastewater. During incineration of the settled floc, 55% of water and 20% of organic matter in the wastewater are vaporized and the compound  $\text{TiO}_{1.42}\text{C}_{0.44}\text{P}_{0.14}$  results. PFW with UV light shows high photocatalytic activity in removing acetaldehyde gas. For example, a medium size ( $25000 \text{ m}^3/\text{d}$ ) wastewater treatment plant could produce 446.5 kg/day of PFW. Thus, this process is efficient and economical not only in terms of removal of organic matter, but also in sludge reduction. As the PFW can be produced in significant quantities in wastewater treatment plants, it can also easily meet demand for  $\text{TiO}_2$  in other applications.

### Acknowledgment

This work is supported by UTS Chancellor's postdoctoral research fellow grant and ARC international-linkage grant.

## References

- (1) Tchobanoglous G.; Burton F.L. Wastewater engineering: treatment, disposal, and reuse, McGraw-Hill, New York, ed. 3, **1991**, pp.15-29.
- (2) Vigneswaran S.; Visvanathan C. Water treatment processes: simple options, CRC press, Florida, **1995**, pp. 78-100.
- (3) Shon H.K.; Vigneswaran S.; Snyder S.A. Effluent organic matter (EfOM) in wastewater: constituents, effects and treatment. *Cri. Rev. Env. Sci. Tec.*, 2006, 36, 327-374.
- (4) DeWolfe J.; Dempsey B.; Taylor M.; Potter J.W. Guidance manual for coagulant changeover, American Water Works Association Press, Denver, 2003, pp. 25-59.
- (5) Molinari R.; Borgese M.; Drioli E.; Palmisano L.; Schiavello M. Hybrid processes coupling photocatalysis and membranes for degradation of organic pollutants in water. *Catal. Today*, 2002, 75, 77-85.
- (6) Chu W.; Wong C.C. The photocatalytic degradation of dicamba in TiO<sub>2</sub> suspensions with the help of hydrogen peroxide by different near UV irradiations. *Water Res.*, 2004, 38, 1037-1043.
- (7) Kaneko M.; Okura I. Photocatalysis: Science and Technology, Springer, Tokyo, 2002, pp 33-38.
- (8) Diebold U. The surface science of titanium dioxide. *Surf. Sci. Rep.*, 2003, 48, 53-229.
- (9) Seo G.T.; Ohgaki S.; Suzuki Y. Sorption characteristics of biological powdered activated carbon in BPAC-MF (biological activated carbon-microfiltration) system for refractory organic removal. *Wat. Sci. Technol.*, 1997, 35, 163-170.
- (10) Shon H.K.; Vigneswaran S.; Ngo H.H. Effect of partial flocculation and adsorption as pretreatment to ultrafiltration in treating wastewater. *AIChE Journal.*, 2006, 52, 207-216.
- (11) WHO. Environmental Health Criteria (24; <http://toxnet.nlm.nih.gov/cgi-bin/sis/search/f?./temp/~THVY88:1>).[the easiest access to this source is by internet], 1982.
- (12) Tonejc A.M.; Djerdj I.; Tonejc A. Evidence from HRTEM image processing, XRD and EDS on nanocrystalline iron-doped titanium oxide powders. *Mat. Sci. Eng. B – Solid*. 2001, 85, 55-63.
- (13) Liao S.C.; Mayo W.E.; Pae K.D. Theory of high pressure/low temperature sintering of bulk nanocrystalline TiO<sub>2</sub>. *Acta. Mater.*, 1997, 45, 4027-4040.
- (14) Suryanarayana C. Nanocrystalline materials. *Int. Mater. Rev.* 1995, 40, 41-64.
- (15) Asiltürk M.; Sayılkan F.; Erdemoğlu S.; Akarsu M.; Sayılkan H.; Erdemoğlu M.; Arpaç E. Characterization of the hydrothermally synthesized nano-TiO<sub>2</sub> crystallite and the photocatalytic degradation of Rhodamine B. *J. Hazard. Mater.* 2006, 129, 164-170.
- (16) Nocun M. Structural studies of phosphate glasses with high ionic conductivity. *J. Non-Cryst. Solids*. 2004, 333, 90-94.
- (17) Asahi R.; Morikawa T.; Ohwaki T.; Aoki K.; Taga Y. Visible-light photocatalysis in nitrogen-doped titanium oxides. *Science* 2001, 293, 269-271.