수처리 티탄염 응집 슬러지에서 생산한 산화티탄의 제조와 특성 조사

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Preparation and Characterisation of Titanium Dioxide Produced from Ti-salt Flocculated Sludge in Water Treatment

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지난 수 년간 본 연구팀은 새로운 티탄염 응집제를 이용하여 폐수를 응집한 후 생산된 슬러지에서 산화티탄을 생산하는 연구를 진행하였다. 티탄염의 응집 효율은 일반적으로 많이 사용되는 철염과 알루미늄염 응집제와 비슷하였으며 슬러지를 소성하여 제조한 산화티탄은 상용 산화티탄보다 더 넓은 표면적과 높은 광촉매 활성을 나타내었다. 산화티탄의 광촉매 활성 향상과 pH를 높이기 위해 응집보조제로서 철, 알루미늄, 칼슘을 사용하여 광촉매 활성이 높은 Fe, Al, Ca 도핑 산화티탄을 제조하였다. 이 기술의 실제 적용 가능성을 확인하기 위하여 염색폐수 파일럿 장치에 적용한 결과, 우수한 유기물 제거 능력과 빠른 응집체 형성이 확인되었다. 염색폐수 슬러지에서 제조한 산화티탄은 높은 유기물 제거 광촉매 활성과 물 광분해에 의해 수소를 생성하였다. 티탄염 응집제와 슬러지에서 제조한 산화티탄의 독성을 *D. magna*로 조사한 결과, 낮은 독성을 확인할 수 있었다. 이 총설은 미래의 슬러지 재활용 기술로 높은 적용 가능성을 가지는 티탄염으로 제조한 산화티탄의 특성을 체계적으로 정리하였다.

During the past few years, titanium salts were investigated as alternative coagulants for the removal of organic matter of different molecular sizes in contaminated water. The flocculation efficiency of Ti-salt was comparable to those of $FeCl_3$ and $Al_2(SO_4)_3$ salts, commonly used coagulants. Incinerated sludge-TiO_2 showed higher surface area and photocatalytic activity than commercially available TiO_2. Metal-doped forms were produced by adding coagulant aids such as iron (Fe-), aluminium (Al-) and (Ca-) calcium salts during Ti-salt flocculation to increase pH. Ca- and Al- doped TiO_2 showed very high photo-catalytic activity compared to Fe-doped TiO_2. When tested in a pilot scale plant for treatment of dye wastewater to check practical feasibility of the novel process, the removal ratio of the chemical oxygen demand was comparable to those of commonly used coagulants but the settling of sludge was faster. The TiO_2 generated after sludge incineration showed a high photocatalytic activity for degradation of volatile organic compounds and increased the rate of hydrogen production by water photosplitting. $TiCl_4$ coagulant and TiO_2 produced from different water sources with different concentrations had low acute toxicity compared to heavy metals and commercial TiO_2 when examined based on *D. Magna* mortality. This paper presents the production, characterisation and the photoactivity of TiO_2 produced from Ti-salt flocculated sludge. Different case studies are discussed to highlighted recent advances in this field.

Keywords: flocculation, titanium salts, flocculated sludge, incineration, TiO₂, photocatalysis, hydrogen production

1. Introduction

1.1. Flocculation for Treatment of Wastewater

Systematic treatment of wastewater for the prevention of pollution and diseases in urban society commenced in the late 19th and early 20th centuries. During the last century, the wastewater treatment was continuously refined to improve its performance and meet stringent disposal standards. The treatment process uses a range of physical, chemical and biological methods. Chemical treatment involves the removal or conversion of contaminants by the addition of particular chemicals
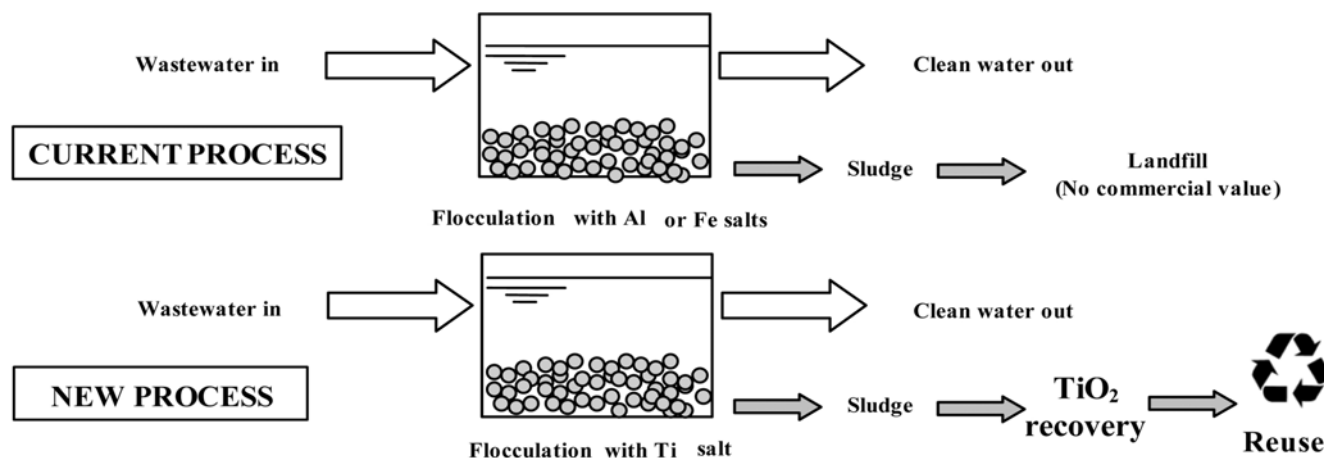
Figure 1. Comparison of the new process described in this review with conventional flocculation.

or by other chemical reactions. Flocculation is one of the most commonly used chemical treatment methods in water and wastewater treatment and causes the coagulation or agglomeration of contaminant particles in large flocs[1]. Flocculation can also be used for the removal of organic matter, which results in the formation of trihalomethane during disinfection. Commonly-used coagulants include: i) aluminium sulfate (72%), ii) iron salts (23%), and iii) polyaluminum chlorides (5%) [2]. However, the flocculation process using these coagulants produces a large amount of sludge, which makes the wastewater treatment process less efficient. Most of the sludge is solid waste from which nothing can be recovered or reused, and thus requires further treatment such as incineration, landfill, etc. Thus, a chemical (coagulant) that produces less amount of sludge or reusable material can offer environmental and economical benefits associated with sludge handling.

1.2. Application of TiO₂

TiO₂ is the most widely used metal oxide in environmental applications for the degradation of waste and for hydrogen generation by photocatalytic water-splitting[3]. This proceeds via an oxidative (electrophilic) attack of high energy (hydroxyl radical, HO·) and leads to complete mineralisation yielding carbon dioxide 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. Photo-induced electrons (e^-) and positive holes (h^+) are produced from TiO₂ by UV light. These charged species can further generate free radicals. The highly oxidising positive hole (h^+) is considered to be dominant oxidising species in the mineralisation process. The usefulness of TiO₂ for degrading contaminants in many applications means that the demand for TiO₂ is greatly increasing. Generally, TiO₂ used for industrial applications is produced by various methods such as: i) sulfate method, ii) chloride method (vapor method), iii) alkoxide method and iv) specific methods[4,5]. However, the problem is that these processes discharge a large amount of wastewater which contains strong acid and chloride/sulfate ions at high concentrations, which makes wastewater treatment difficult without cost-intensive advanced processes.

1.3. Objectives

To resolve the above problems, a new process which can economically recover valuable TiO₂ from synthetic wastewater (SWW) has been developed[5]. A large amount of functional TiO₂ was produced from SWW sludge generated by the Ti-salt flocculation. In addition, this novel flocculation process simultaneously reduced problems of strong acid and high concentrations of chloride ions by using a small amount of Ti-salt as a coagulant to treat a large volume of wastewater. The schematic diagram of benefits of the process is shown in Figure 1. This review aims to investigate the past, present and future experience and knowledge of the preparation of TiO₂ produced from Ti-salt flocculated sludge.

2. Ti-salt Coagulant for Water Treatment

The possibility of using titanium compounds as a coagulant in water treatment was first investigated by Upton and Buswell[6]. They found that titanium sulfate ($Ti(SO_4)_2$) was better in fluoride removal due to quadrivalent cations instead of trivalent aluminiums or iron ions. They also claimed that ilmenite extract gave much better coagulation in coloured water highly contaminated with colloidal matter and dissolved salts than aluminium or ferric sulfates. Furthermore, titanium salts appeared to be feasible from the standpoint of cost and the pH range for good floc formation. The titanium floc formed more rapidly in a bulkier condition. On the other hand, titanium sulfate showed no advantage over aluminium sulfate in fluoride removal but removed colour from water more efficiently. Lokshin and Belikov[7] also investigated the Ti salts flocculation. Wastewater could efficiently be purified by removal of fluoride ions with titanium (IV) compounds, especially with hydrated oxotitanium sulphate. They found that concentration of the sulfate ions in the purified water after titanium sulfate flocculation did not exceed the permissible limit at the optimum doses of wastewater purification.

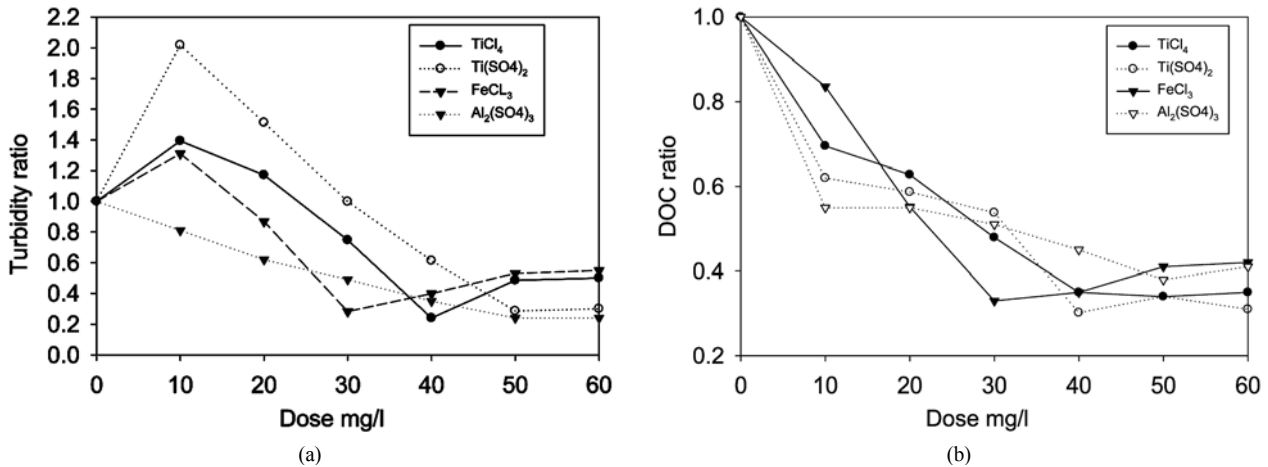The effectiveness of Ti-salts has been studied by several researchers.

Figure 2. Variation in residual turbidity ratio and residual DOC ratio as a function of coagulants doses.

Shon et al.[5] recently proposed a novel process to utilise the Ti-salt coagulant to recover a useful byproduct. Removal of organic matter of different molecular sizes by Ti-salt flocculation was similar to those of the most widely-used Fe- and Al-salt flocculation. They found that the removals of organic matter at optimum doses by Fe, Al and Ti-salt flocculation was 73% (13.8 Fe-mg/L), 70% (16 Al-mg/L) and 70% (9.8 Ti-mg/L), respectively. The mean size of Ti-, Fe- and Al-salt flocs was 47.5 μm, 42.5 μm and 16.9 μm, respectively. The settleability of flocs by Ti-salt coagulant was better than that by $FeCl_3$ coagulant and $Al_2(SO_4)_3$. Okour et al.[8] also investigated the flocculation with $TiCl_4$ and $Ti(SO_4)_2$ using synthetic wastewater in terms of turbidity, dissolved organic carbon (DOC), UV absorbance at 254 nm (UVA_{254}), colour. Ti-salts were compared with $FeCl_3$ and $Al_2(SO_4)_3$. They found that $TiCl_4$ showed better turbidity removal while $Ti(SO_4)_2$ showed the highest reduction of UV absorbance and colour at all pH range. Compared to aluminium and iron salt coagulants, $TiCl_4$ and $Ti(SO_4)_2$ were found to have similar organic removal up to 60~67% and similar molecular weight removal of organic matter (Figure 2). The decantability of the settled flocs was higher for $TiCl_4$, $Ti(SO_4)_2$ and $FeCl_3$ than for $Al_2(SO_4)_3$. It can be concluded that Ti-salt coagulants have a high potential to apply to water treatment plants. Kim et al.[9] studied the flocculation of dye wastewater (DWW) using $TiCl_4$ and ferric sulfate ($FeSO_4$). Results showed that 77.6% of COD_{Mn} was removed from DWW when $FeSO_4$ was used as a coagulant while $TiCl_4$ degraded 75.9% of COD_{Mn}. On the other hand, the precipitation efficiency was better with $TiCl_4$ than with $FeSO_4$.

3. Resource Recovery with Ti-salt Flocculated Sludge

The settled flocs (sludge) produced by $Al_2(SO_4)_3$, $FeCl_3$ and $TiCl_4$ flocculation were recycled with a novel flocculation process, by which cost of waste disposal can significantly be reduced, environment and public health can be protected economically useful by-products can be obtained[10]. Figure 3 shows XRD images to identify the particle crystalline structure after calcination of the settled floc at different temper-

atures ranging from 100 to 1000 ℃. After $TiCl_4$ flocculation, the anatase pattern was found at temperatures higher than 600 ℃ (Figure 2a). At lower temperatures, remaining organic matter interfered TiO_2 production. At 1000 ℃, the anatase structure changed to rutile. Although there are a lot of different compounds in synthetic wastewater, genuine TiO_2 crystalline structure was found. In the case of the settled floc after $FeCl_3$ flocculation, the incinerated flocs were found to have different structures (hematite (Fe_2O_3)) and grattarolaite (($Fe_3PO_4)O_3$ or Fe_3PO_7) (Figure 2b). On the other hand, only Al_2O_3 was made at 1000 ℃ after $Al_2(SO_4)_3$ flocculation (Figure 2c). Interestingly, berlinite ($AlPO_4$) could not be made with Al-flocs. These metal oxide by-products produced in such way are efficient and economical not only in terms of removal of organic materials in wastewater but also in sludge reduction. As significant amount of metal oxides can be produced at wastewater treatment plants, they can also easily meet demands for different metal oxides in other applications such as environmental photocatalysis. Due to a wide range of applications of TiO_2 this review will mainly focus on preparation and characterisation of TiO_2 produced from sludge.

4. Preparation and Characterisation of TiO_2 Produced from Sludge After Flocculation

The mechanism of TiO_2 preparation from sludge after Ti-salt flocculation has not been fully explained because flocculation is a very complex phenomenon. However, it can generally be explained as shown in Figure 4. $TiCl_4$, changes to $TiOCl_2$ in an aqueous phase and the $TiOCl_2$ hydrolyses to $Ti(OH)_4$ depending on pH of the system. Negatively-charged organic matter is absorbed by $Ti(OH)_4$, and organic matter is agglomerated with the $Ti(OH)_4$ into large flocs. During incineration of the settled floc, 55% of water and 20% of organic matter in the wastewater are vaporized and result in the formation of $TiO_{1.42}C_{0.44}P_{0.14}$ (obtained from X-ray photoelectron spectroscopy analysis).

The crystallite size of the TiO_2 produced from the sludge after incineration of 600 ℃ with synthetic wastewater was 6.0 nm (Figure 5).
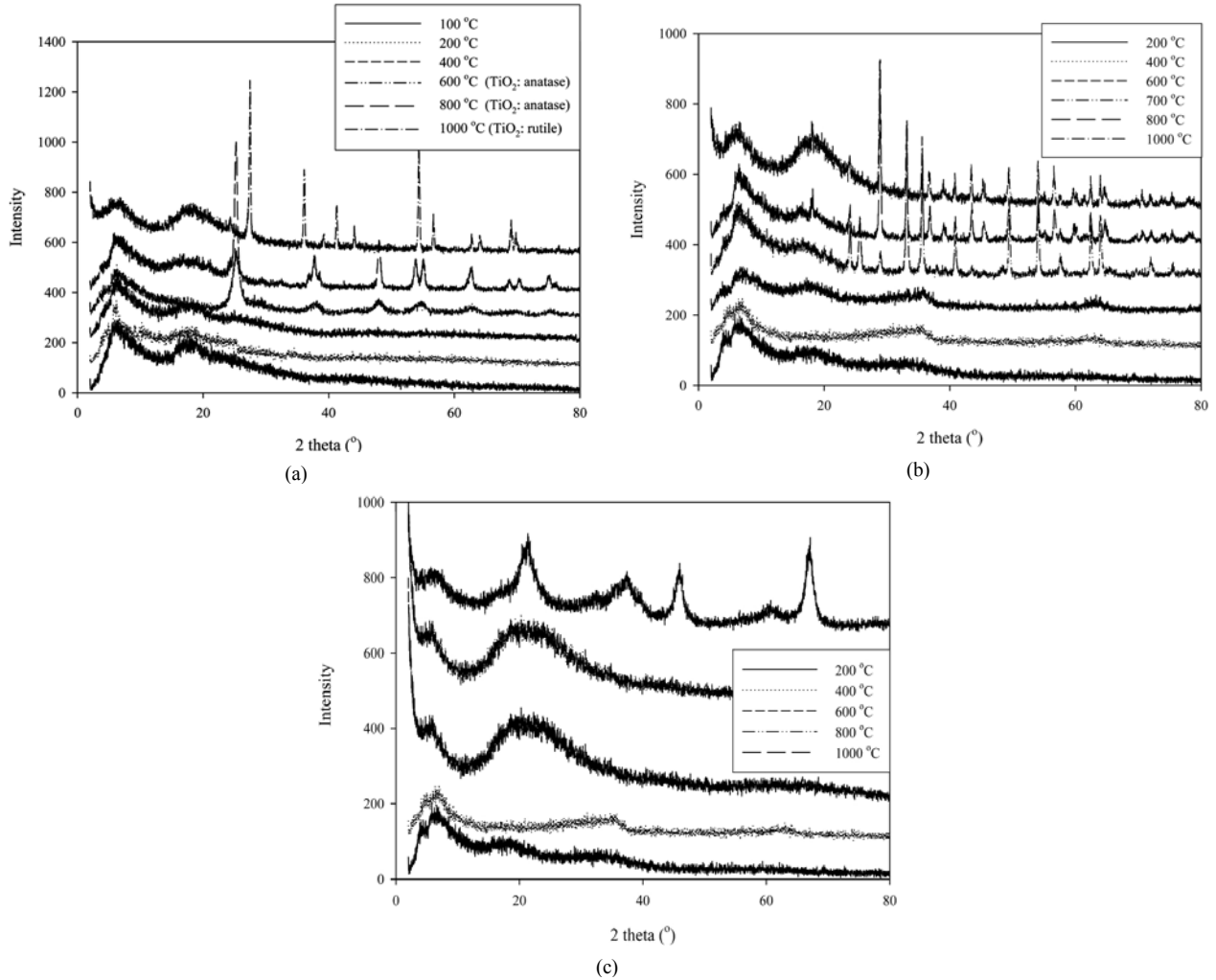
(a)

(b)

(c)

Figure 3. XRD images (a) of the settled floc after TiCl₄ flocculation, (b) of the settled floc after FeCl₃ flocculation and (c) of the settled floc after Al₂(SO₄)₃ flocculation by calcination at different temperatures.
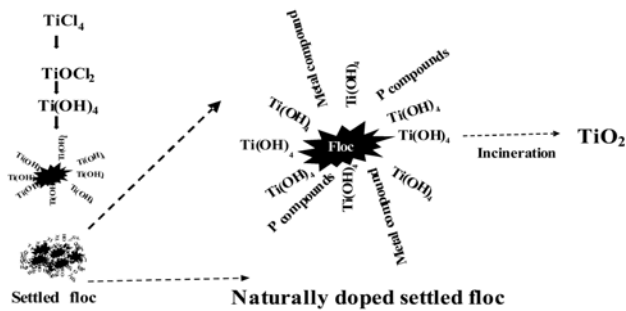

Figure 4. Mechanism of the floc formation by TiCl₄ flocculation and TiO₂ production.

The specific surface area of the functional TiO_2 was 76.3 m²/g, which was higher than that of TiO_2-P25, the most widely used commercial photocatalyst. Based on the scanning electron microscopy/energy dispersive X-ray (SEM/EDX) results, C and P atoms were found to be mainly doped in/on TiO_2. These atoms help the improvement of TiO_2

photoactivity. The atomic percentage of Ti, O, C and P of the TiO_2 was 26.9 : 51.5 : 15.8 : 5.8[5]. The photocatalytic property of the TiO_2 was investigated for the photodecomposition of gaseous acetaldehyde and was then compared to that of the TiO_2-P25 photocatalyst (Figure 6). The functional TiO_2 was better in all aspects than the commercially available TiO_2-P25 and up to 20% better for the removal of acetaldehyde than the TiO_2-P25 under UV irradiation. After 90 minutes of the photocatalytic reaction, the functional TiO_2 photocatalyst removed the majority of acetaldehyde. Moreover, formation of dioxin-like polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzo-furans (PCDFs) in the residue during incineration of wastewater and their removal was investigated. The removal of PCDDs, PCDFs and dioxin-like PCBs was 27.3%, 70.7% and 27.5%, respectively by the TiO_2 thermal catalyst. This suggests that the TiO_2 produced from sludge during incineration also led to preferential removal of PCDFs.
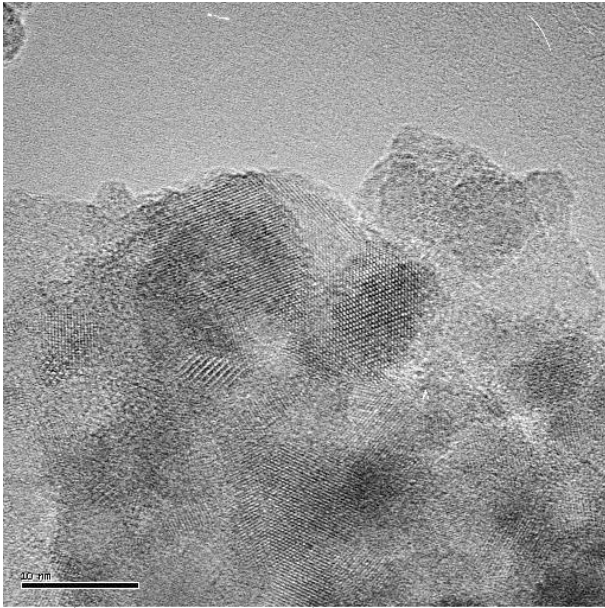
Figure 5. High resolution transmission electron microscope image of TiO₂ produced from sludge with Ti-salt flocculation.
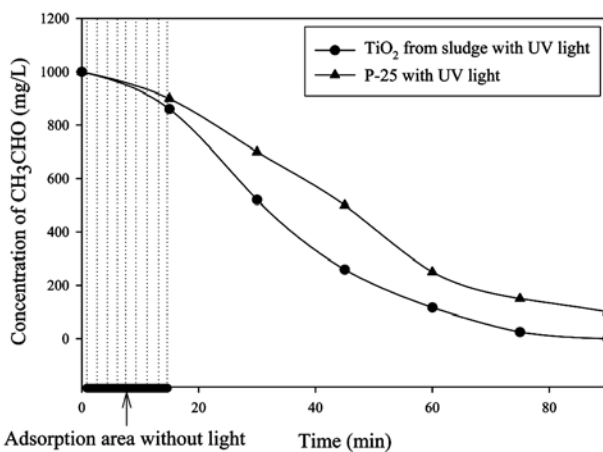

Figure 6. Variation of acetaldehyde concentration with irradiation time (initial concentration = 1000 mg/L; UV irradiation = black light three 10 W lamps).

5. Preparation and Characterization of TiO₂ from Sludge Produced by TiCl₄ Flocculation with FeCl₃, Al₂(SO₄)₃ and Ca(OH)₂ Coagulant Aids in Wastewater

The pH value of the supernatant at the optimum concentration of 8.4 Ti-mg/L of TiCl₄ flocculation was low (pH 3.25), and was lower than those of Fe and Al salt flocculation[5]. The problem could be solved by post-treatment after TiCl₄ flocculation. The post-treatment would be an addition of sodium hydroxide (NaOH) to neutralize the pH value. Alternatively, coagulant aids such as FeCl₃, Al₂(SO₄)₃ and Ca(OH)₂ could be simultaneously added during flocculation with TiCl₄. Incineration of co-flocculated sludge would produce Fe-, Al- and Ca-doped

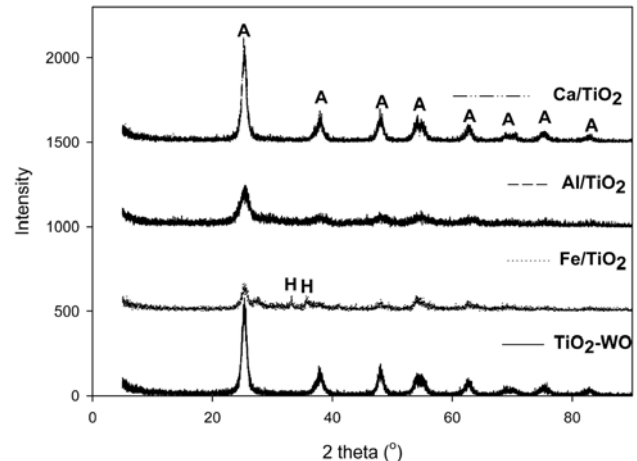**Figure 7. XRD patterns of TiO₂-WO, Fe/TiO₂, Al/TiO₂ and Ca/TiO₂ produced from incineration of the settled floc at 600 ℃ (A: anatase phase (TiO₂); H: hematite (α-Fe₂O₃)).**

TiO₂.

Shon *et al.*[10] studied on the variation in the pH after Ti-salt flocculation together with Fe-salt, Al-salt and Ca-salt flocculation. They also investigated the property of TiO₂ doped with Fe, Al and Ca compounds. They found that all the three coagulant aids increased the pH value. The Fe- and Al-salt coagulants aids increased the pH range only by a small amount (about pH 5), while the Ca-salt coagulant significantly increased the pH (close to neutral pH value). This is due to the input of OH⁻ ions from Ca(OH)₂. The DOC removal increased with increase in the concentration of coagulant aids. The DOC removal was 70% to 72% for Fe and Al salt concentration of 6.9 Fe-mg/L and 8 Al-mg/L, respectively. Ca-salt concentration of 15 Ca-mg/L achieved DOC removal of 70%. This can be explained in terms of the charge of the cations. The higher the charge of a cation, the stronger is its effect on the zeta-potential. The higher the valance is, the higher the coagulative power.

TiO₂-WO refers to TiO₂ without any coagulant aids and Fe/TiO₂, Al/TiO₂ and Ca/TiO₂ refers to TiO₂ obtained from TiCl₄ coagulant together with Fe-, Al- and Ca-salt coagulant aids at the different optimum concentrations, respectively. Figure 7 presents the XRD patterns of TiO₂-WO, Fe/TiO₂, Al/TiO₂ and Ca/TiO₂ incinerated at 600 ℃. The TiO₂-WO, Fe/TiO₂, Al/TiO₂ and Ca/TiO₂ show mostly the anatase phase. The XRD pattern on the Fe/TiO₂ showed a peak of hematite (α-Fe₂O₃). The peak of low intensity, due to an iron-TiO₂ mixed phase, of composition Fe₂TiO₅, crystallized poorly in very small grain sizes evidenced by the remarkable enlargement of the diffraction peak, as detected on the Fe/TiO₂. A crystalline phase containing Al atoms (α-Al₂O₃ and Al₂TiO₅) was not observed in the Al/TiO₂. This is due to low concentrations of Al₂O₃ and/or a substitute site (Al³⁺) for a Ti⁴⁺ ion. Since the ionic radius for Al and Ti are similar (0.68 Å for Al³⁺), Al can occupy a regular cation position, forming a substitutional solid solution. In addition, Al species dissolve well into the TiO₂ crystal. The crystalline phase containing Ca atoms (CaO and CaTiO₃) was not observed on the Ca/TiO₂. To sum up, different crystalline phases such
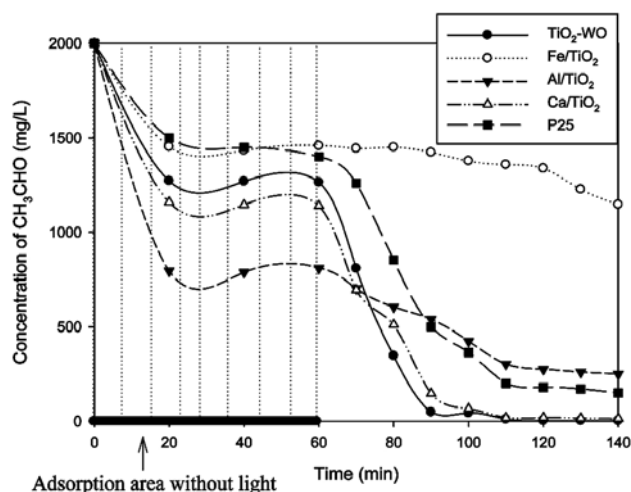
Figure 8. Variation of acetaldehyde concentration with UV irradiation time (TiO₂ concentration = 1 g; initial concentration = 2000 mg/L; UV irradiation = black light three 10 W lamps).

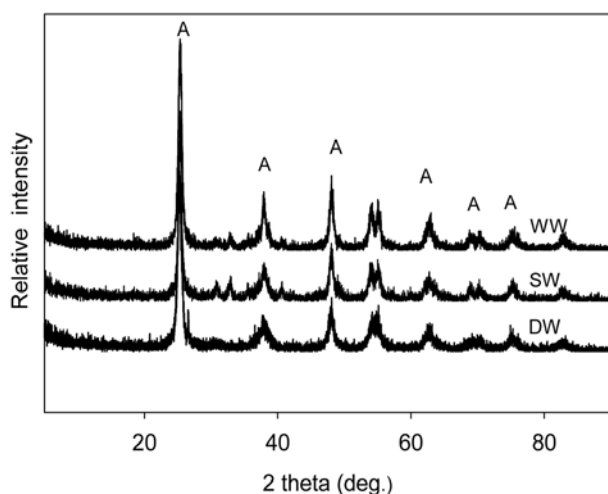**Table 1. Crystallite Size and BET Surface area of TiO₂ Produced from Different Water Sources**

TiO₂	Crystallite size (nm)	Surface area (m₂/g)
DW	13	90.2
WW	15	103.5
SW	40	68.1
P-25	25	42.3

Table 2. EDX results of TiO₂ from DW, WW and SW compounds as atomic and weight percentages

	Atomic %			Weight %		
	C	O	Ti	C	O	Ti
DW	3.87	65.92	27.65	1.86	42.2	53.05
WW	4.82	59.58	32.19	2.18	35.95	58.14
SW	4.62	67.08	24.57	2.3	44.55	48.85

moval by adsorption showed the following order: Al/TiO₂ (136 m²/g) >> Ca/TiO₂ (116 m²/g) > TiO₂ (122 m²/g) > Fe/TiO₂ (77 m²/g) ≥ TiO₂-P25 (50 m²/g). The majority of acetaldehyde with TiO₂-WO and Ca/TiO₂ was completely removed under UV irradiation within 40 minutes. TiO₂-P25 and Al/TiO₂ led to a high photoactivity with the removal of 90%. However, at a high iron concentration (6.5 at.%), acetaldehyde removal by photo-oxidation under UV irradiation was marginal. Wang et al.[12] reported that formation of Fe₂O₃ and Fe₂TiO₅ at high incineration temperature (600∼800 ℃) resulted in a decrease of photocatalytic activity. Hung et al.[13] reported that the optimum concentration of iron ions was 0.005% (Fe/Ti) and this enhanced gaseous dichloromethane removal. When the concentration of iron ions was high, the iron ions became recombination centres for the electron-hole pairs and reduced the photocatalytic activity. Under visible light, the photo-decomposition of acetaldehyde using TiO₂-WO, Fe/TiO₂, Al/TiO₂, Ca/TiO₂ and TiO₂-P25 was marginal.

6. TiO₂ Production from Ti-salt Flocculation with Drinking Water, Wastewater and Seawater Resources

In order to investigate a real application of Ti-salt flocculation with drinking water (DW), wastewater (WW) from biologically treated sewage effluent and seawater (SW), the characteristics of TiO₂ produced from sludge of Ti-salt flocculation were studied by Okour et al.[14]. Figure 9 shows XRD patterns from DW, WW and SW. XRD results showed that the anatase structure was predominant from different water sources.

Table 1 shows the characteristics of TiO₂ produced from DW, WW and SW in terms of crystallite size and BET surface area and TiO₂ was compared with P25. The crystallite size of TiO₂ from DW, WW, SW and TiO₂-P25 was 13, 15, 40, and 25 nm, respectively[15]. The difference in crystallite size among different water sources was probably due to impurities in the flocculated sludge after Ti-salt flocculation and incineration. The BET surface area of TiO₂ nanoparticles from DW,

Figure 9. XRD patterns of TiO₂ produced from DW, WW and SW sources.

as α-Al₂O₃ and Al₂TiO₅ from Al/TiO₂ and CaO and CaTiO₃ from Ca/TiO₂ were not found. On the other hand, the XRD pattern of α-Fe₂O₃ from Fe/TiO₂ was observed. The crystalline size of different TiO₂ was calculated using Scherrer's formula[11]. The crystallite size of TiO₂-WO, Fe/TiO₂, Al/TiO₂ and Ca/TiO₂ was approximately 11 nm, 6 nm, 8 nm and 11 nm, respectively. The intensity of the anatase phase on Fe/TiO₂ and Al/TiO₂ significantly decreased. This suggests that the Fe and Al species inhibited a crystalline growth. On the other hand, the intensity of the anatase phase on the Ca/TiO₂ was similar to that on the TiO₂-WO.

The photocatalytic property of TiO₂-WO, Fe/TiO₂, Al/TiO₂ and Ca/TiO₂ was examined under irradiation of UV and visible light for the photo-decomposition of gaseous acetaldehyde (Figure 8). TiO₂-P25 was used to compare the photocatalytic activity with other TiO₂. The concentration of acetaldehyde was measured by gas chromatography. The re-
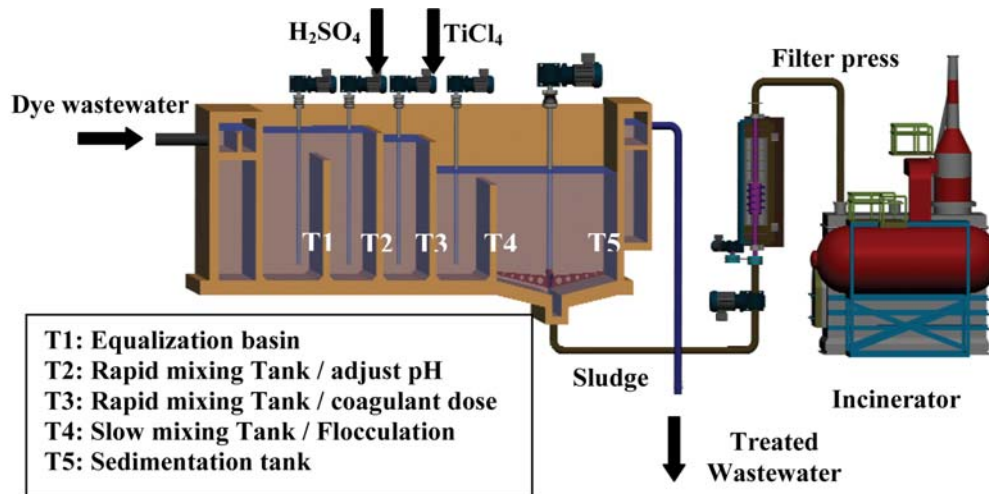
Figure 10. Schematic diagram of the pilot-scale flocculation basin to produce TiO₂ from sludge with DWW.

WW, SW and TiO₂-P25 was 90.2, 103.5, 68.1 and 42.3 m²/g, respectively.

TiO₂ from DW, SW and WW was mainly doped with carbon atoms. The atomic percentages of carbon atoms were less than 5% (Table 2). Many other elements such as Na, Mg, Si, S, K, Ca, and Al were also detected but they were of low insignificant atomic and weight percentage < 1.35%. The concentrations of different doping elements on TiO₂ depend on water characteristics from different water sources.

7. Effect of Washing TiO₂ Prepared from Ti-salts Flocculated Wastewater Sludge

Due to the TiO₂ production from different water sources present in many different organic/inorganic compounds, it is important to investigate the washing effect of TiO₂ produced from sludge. El Saliby *et al.*[16] examined the effect of washing on TiO₂ produced from sludge of Ti-salt flocculation with synthetic wastewater. The TiO₂ produced was washed using HCl, NaOH and pure water to determine the effect of washings on adsorption and photocatalytic oxidation of acetaldehyde. The extent of photooxidation of synthetic wastewater by the produced TiO₂ after different washings showed several benefits. Washed TiO₂ improved the adsorption and the photocatalytic ability in decomposing acetaldehyde under UV-irradiation. TiO₂ after basic washing was fast in decomposing organic compounds in water phase in terms of organic removal. Similarly, TiO₂ after acidic washing was better than as-prepared TiO₂.

8. Verification of a Pilot-scale Ti-salt Flocculation to Produce TiO₂ with Dye Wastewater (DWW)

The novel process has been successfully developed using a lab-scale study. A verification of a pilot-scale experience requires to investigate and to improve process performance in realistic operational conditions, using different raw waters. Kim *et al.*[9] conducted the pilot-scale process to demonstrate feasibility of the novel process. Figure 10
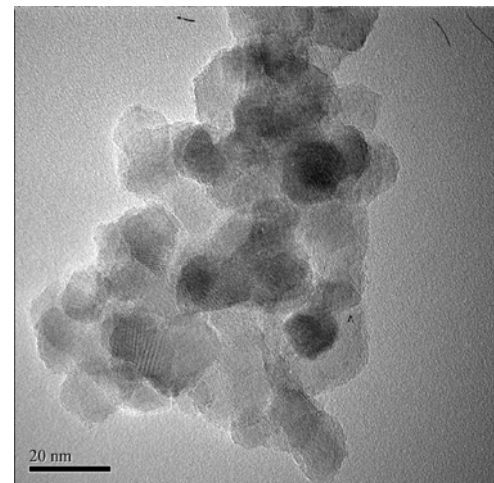

Figure 11. High-resolution transmission electron microscope image of TiO₂-DWW.

shows the schematic diagram of the pilot-scale flocculant basin. The basin consisted of equalization, rapid mixing, slow mixing and sedimentation tanks and treated 1 m³/h of dye wastewater. During the rapid mixing time, pH was adjusted and a coagulant was added at 100 rpm. After flocculation, the settled floc was collected from the sedimentation tank and then the floc went through a filter press to dewater the settled floc. Capacity of the filter press was 1.2 m³/h. The dewatered sludge was dried in rotary furnace at 300 ℃. The dry sludge was incinerated at 600 ℃ to remove organic content of the sludge.

XRD patterns were drawn to identify the structure of TiO₂ from dye wastewater (TiO₂-DWW). Sludge generated from the flocculation of DWW using TiCl₄ was incinerated at 600 ℃ to produce TiO₂-DWW. XRD results showed that the anatase structure was predominant in TiO₂-DWW. Transmission electron microscopy image showed that 15 ~20 nm anatase particles are present after incineration at a temperature of 600 ℃ (Figure 11). Table 3 shows SEM/EDX results for TiO₂-DWW. TiO₂-DWW was mainly doped with carbon atoms. Many

Table 3. Atomic fraction of TiO₂-DWW and TiO₂-P25

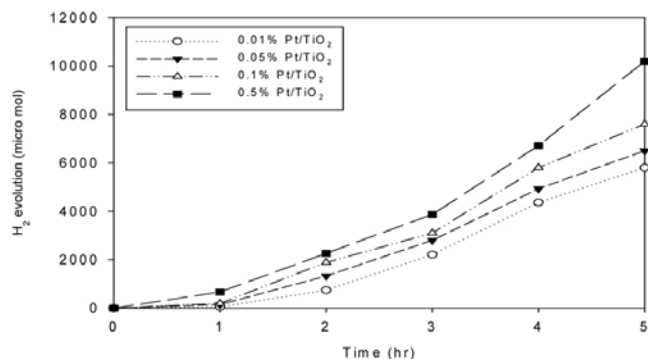| Element	Atomic% of TiO₂-DWW after TiCl₄ flocculation	Atomic% of TiO₂-P25
C	5.09	-
O	62.80	76.98
Na	0.56	-
Si	1.12	-
Ti	30.20	23.02
etc	0.23	-
Total	100	100

Figure 12. Effect of Pt deposition concentration on DWT for H₂ production by photocatalytic reforming of methanol (6 vol%).

other contaminants were recorded such as Na and Si but they were of insignificant atomic percentage (<1.2%). The photocatalytic oxidation of acetaldehyde was studied with TiO₂-DWW. TiO₂-P25 was used as a commercial TiO₂ reference for assessing the results obtained from TiO₂-DWW. Acetaldehyde was adsorbed onto TiO₂-DWW surface in dark conditions for 60 minutes (lamp off). The removal after 60 minutes adsorption was very low and the concentration (around 1900 ppm) was slightly lower than the initial concentration (2000 ppm) for both TiO₂-DWW and TiO₂-P25. When UV lamps were turned on, a sharp drop of acetaldehyde concentration was observed and complete oxidation was achieved after 140 min of UV-irradiation. Similar trends were found between TiO₂-DWW and TiO₂-P25 in terms of photocatalytic oxidation of acetaldehyde, which indicates the potential use of TiO₂-DWW for decomposing volatile organic contaminants.

9. Hydrogen Production from TiO₂ Produced from the Incineration of DWW Flocculated Sludge after Ti-salt Flocculation

The photosplitting of water can be divided into: i) the photoelectrochemical system[17-20] and ii) and the photocatalytic suspension system[21,22]. Extensive studies focused in the past decade on improving the production of hydrogen by using the photocatalytic suspension system with TiO₂ as catalyst[21,23,24]. Presently, the energy conversion efficiency from solar to hydrogen by TiO₂ photocatalytic water-splitting is still low, mainly due to the: i) recombination of photo-generated electron/hole pairs; ii) fast backward reaction (recombination of hydrogen and oxygen into water); and iii) inability to utilize visible light[25].

Many efforts have been made to improve the photocatalytic suspension system through noble metal loading on TiO₂ surface[26-30] or the use of organic solvents as "sacrificial reagents"[27,29,31-33]. However, Ni et al.[25] reported that hydrogen production from pure water-splitting is difficult to achieve even if noble metal loading can reduce recombination to some extent. This is mainly due to: i) recombination cannot be completely eliminated; ii) backward reaction of H₂ and O₂ to form H₂O is thermodynamically favourable. Therefore, the addition of sacrificial electron donor (organic compounds) which becomes progressively oxidized toward CO₂ by consuming photogenerated holes and/or oxygen will increase hydrogen production[34]. High rate of hydrogen production was reported by Chiarello et al. (2008) when using Au-modified titanium dioxide prepared by flame spray pyrolysis for pure water photosplitting. Further increase in H₂ production was achieved with the addition of methanol to the suspension. Similarly, the production of H₂ via methanol/water photodecomposition was enhanced with Cu/TiO₂ compared to TiO₂[31]. The production of H₂ reached 13500 μmol after methanol/water photodecomposition for 10 h over 10% mol Cu/TiO₂ catalyst. Pastoura et al.[34] found that enhanced hydrogen production process is directly related to the amount of sacrificial reagent present in the suspension of Pt/TiO₂ and water. After the complete oxidation of the sacrificial reagent they recorded a drop of the rate of hydrogen production to values comparable to those obtained from pure water.

Shon et al.[35] investigated TiO₂-DWW which was produced from the incineration of dye wastewater flocculated sludge to produce H₂ energy. They doped TiO₂-DWW with Pt metal to increase H₂ production. Figure 12 shows the variation of H₂ production by photocatalytic reforming of methanol in relation to Pt deposition concentration on TiO₂-DWW. To prevent the recombination, TiO₂ produced from sludge was doped with Pt metal to hold electrons. These Pt-deposited TiO₂ nanoparticles were placed in the photoreactor containing pure water and methanol. As the doping concentration of Pt deposited on TiO₂ produced from DWW sludge increased from 0.01% to 0.5%, the H₂ amount increased. The H₂ amount with 0.5% Pt/TiO₂ was 10201 μmol. The increase in H₂ production rate in relation to the increased Pt deposition on TiO₂ may be due to effective loading of the co-catalyst (Pt) on the catalyst (TiO₂) and the formation of increased Schottky barriers (potential barrier formed at a metal-TiO₂ junction which has rectifying characteristics) between Pt and TiO₂[33].

10. Aquatic Toxicity Evaluation of TiO₂ Nanoparticle Produced from Sludge of TiCl₄ Flocculation of Wastewater and Seawater

Flocculation using titanium salt as coagulant is efficient and economical because the flocculated sludge can be recycled to produce a valuable byproduct of TiO₂ nanoparticles. However, the toxicity of Ti-salt is not known to be safely used in water treatment. Aquatic tox-
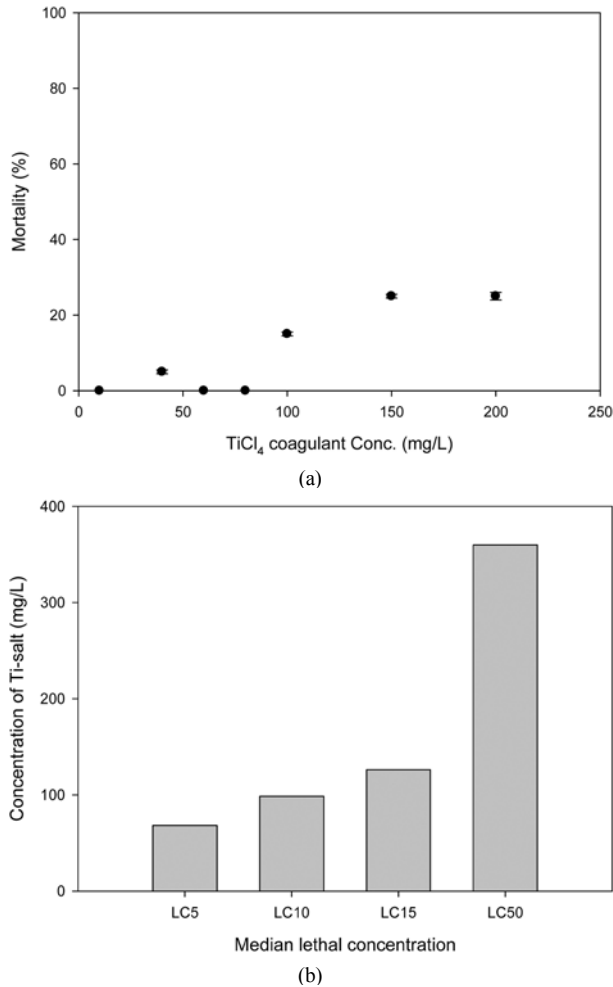
(a)

(b)

Figure 13. (a) Mortality of *D. magna* on exposure to TiCl₄ coagulant and (b) median lethal concentration of TiCl₄.

icity of the TiCl₄ flocculation processes was investigated to assess the environmental safety[15]. *D. magna* and V. *fischeri* bioassays were carried out to analyze the toxicities of supernatant after TiCl₄ flocculation and recovered TiO₂ nanoparticles from the sludge.

Aquatic toxicity of TiCl₄ coagulant was investigated using *D. magna* mortality with different TiCl₄ concentrations (Figure 13). TiCl₄ ranging from 0 mg/L to 200 mg/L concentration was exposed to *D. magna*. The exposure with TiCl₄ concentration of less than 80 mg/L experienced no fatalities. However, TiCl₄ concentrations of 100 mg/L exhibited 15%, and 150 mg/L and 200 mg/L both exhibited 25% mortality. Median lethal concentration of TiCl₄ was investigated in terms of LC5, LC10, LC15 and LC50. The LC5, LC10, LC15 and LC50 of TiCl₄ were 68.1 mg/L, 98.4 mg/L, 126.1 mg/L and 359.9 mg/L, respectively. Compared to other heavy metals such as copper (Cu), lead (Pb) and zinc (Zn), the LC 50 of TiCl₄ exhibited higher concentration. This means that TiCl₄ coagulant has low acute toxicity in water compared to above mention heavy metals.

The aquatic toxicity, *D. magna* mortality, of TiO₂ produced from different waster sources was investigated by Lee *et al.*[15]. TiO₂ con-
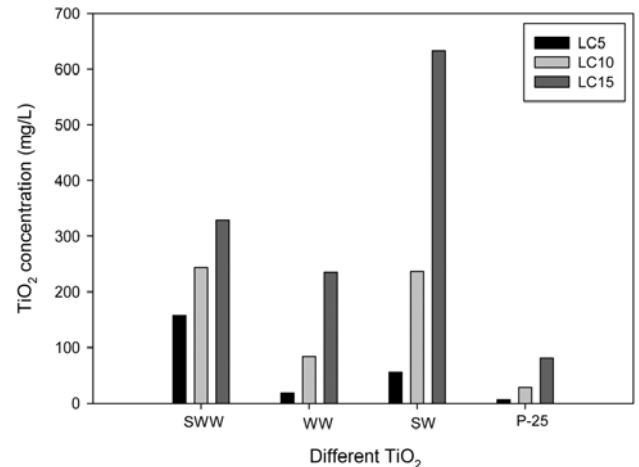

Figure 14. Concentration values of LC5, LC10 and LC15 to TiO₂ produced from SWW, WW and SW.

centration was varied from 0 mg/L to 200 mg/L. The maximum mortality of TiO₂ produced from SWW, WW from biologically treated sewage effluent and SW was less than 15%, while that of TiO₂-P25 was 25% at the concentration of 100 mg/L. As all the TiO₂ particles indicated low mortality, the LC50 was not found. Therefore, LC5, LC10 and LC15 were compared using USEPA Probit analysis program (Figure 14). The commercially available P-25 TiO₂ showed lower values of LC5 (5.9 mg/L), LC10 (28.4 mg/L) and LC15 (81.3 mg/L) compared to TiO₂ produced from SWW, WW and SW. This result clearly indicates that TiO₂ nanoparticles produced from SWW, WW and SW have low acute toxicity in aqueous condition. This is in good agreement with the previous studies[36,37]. Johnson *et al.*[36] reported that mean concentration values of TiO₂ required to immobilize 50% of *D. magna* was more than 1 g/L. Lovern and Klaper[37] found that mortality with sonicated TiO₂ was less than 9% and the LC50 was zero for the sonicated TiO₂ solution. However, when exposed to the filtered TiO₂ with 0.22 μm microfilter, the LC50 was calculated to be 5.5 mg/L with the lowest observable effect concentration (2.0 mg/L) and no observable effect concentration (1 mg/L). Thus, when the filtered TiO₂ was used, more attention needed to be paid in assessing the acute toxicity.

11. Conclusions

The novel flocculation process successfully utilized the sludge produced by Ti-salt, FeCl₃ and Al₂(SO₄)₃ flocculation through incineration to reduce the cost of waste disposal and produce Ti-, Fe- and Al-oxides. The incineration of the flocculated sludge from Ti-salt flocculation at 600 ℃ produced a useful byproduct (TiO₂). In another study, drinking water, seawater and wastewater flocculation was investigated to produce different types of TiO₂. In general, TiO₂ from different water sources was mainly doped with 3∼5% carbon atoms, while TiO₂ produced from synthetic wastewater was doped with C and P atoms to up to 20%. Anatase structure was predominant for all TiO₂

produced from different water sources, while the surface area of TiO_2 from synthetic wastewater, wastewater and seawater was 76.3, 103.5 and 68.1 m^2/g, respectively. Interestingly, the photocatalytic activity of TiO_2 produced from synthetic wastewater was higher than that of commercial P-25 under UV light for the photodecomposition of gaseous acetaldehyde.

On the other hand, coagulant aids such as iron, aluminum and calcium salts were added during Ti-salt flocculation to increase the pH after Ti-salt flocculation and to produce Fe-, Al- and Ca-doped TiO_2. Dissolved organic carbon (DOC) removal increased with the increase in coagulant aids concentrations and reached up to 72% at the optimum doses. Ca- and Al-doped TiO_2 effectively worked as photocatalysts under UV light.

Pilot scale plant flocculation using $TiCl_4$ to treat dye wastewater was investigated. The organic removal was relatively similar to the one obtained from conventional coagulants but the settling of $TiCl_4$ sludge was faster which made the subsequent separation process easier. The photocatalytic activity of TiO_2 from dye wastewater was comparable to that of commercial P-25 under UV light.

Finally, *D. Magna* mortality results showed very low acute toxicity effect for $TiCl_4$ coagulant and TiO_2 produced from different water sources. Accordingly, the use of Ti-salts has a significant environmental and economical effect that can resolve many problems associated with water treatment.

Acknowledgements

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