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


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(Received May 28, 2009)

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 FeCl₃ and Al₂(SO₄)₃ salts, commonly used coagulants. Incinerated sludge-TiO₂ showed higher surface area and photocatalytic activity than commercially available TiO₂. 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 TiO₂ showed very high photocatalytic activity compared to Fe-doped TiO₂. 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 TiO₂ 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. TiCl₄ coagulant and TiO₂ produced from different water sources with different concentrations had low acute toxicity compared to heavy metals and commercial TiO₂ when examined based on D. Magna mortality. This paper presents the production, characterisation and the photoactivity of TiO₂ 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.
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(SO₄)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.
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 FeCl₃ coagulant and Al₂(SO₄)₃. Okour et al. [8] also investigated the flocculation with TiCl₄ and Ti(SO₄)₂ using synthetic wastewater in terms of turbidity, dissolved organic carbon (DOC), UV absorbance at 254 nm (UVA₂₅₄), colour. Ti-salts were compared with FeCl₃ and Al₂(SO₄)₃. They found that TiCl₄ showed better turbidity removal while TiCl₄ showed the highest reduction of UV absorbance and colour at all pH range. Compared to aluminium and iron salt coagulants, TiCl₄ and Ti(SO₄)₂ were found to have similar organic removal up to 60–67% and similar molecular weight removal of organic matter (Figure 2). The decontamination of the settled flocs was higher for TiCl₄, Ti(SO₄)₂ and FeCl₃ than for Al₂(SO₄)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 TiCl₄ and ferric sulfate (FeSO₄). Results showed that 77.6% of CODₜₙₜₙ was removed from DWW when FeSO₄ was used as a coagulant while TiCl₄ degraded 75.9% of CODₜₙₙ. On the other hand, the precipitation efficiency was better with TiCl₄ than with FeSO₄.

3. Resource Recovery with Ti-salt Flocculated Sludge

The settled flocs (sludge) produced by Al₂(SO₄)₃, FeCl₃ and TiCl₄ 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 temperatures ranging from 100 to 1000 °C. After TiCl₄ flocculation, the anatase pattern was found at temperatures higher than 600 °C (Figure 2a). At lower temperatures, remaining organic matter interfered TiO₂ production. At 1000 °C, the anatase structure changed to rutile. Although there are a lot of different compounds in synthetic wastewater, Ti-salt crystalline structure was found. In the case of the settled floc after FeCl₃ flocculation, the incinerated flocs were found to have different structures (hematite (Fe₂O₃)) and grattarolite ((Fe₃PO₄)O₃ or Fe₃PO₇) (Figure 2b). On the other hand, only Al₂O₃ was made at 1000 °C after Al₂(SO₄)₃ flocculation (Figure 2c). Interestingly, berlinite (AlPO₄) 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 TiO₂ this review will mainly focus on preparation and characterisation of TiO₂ produced from sludge.

4. Preparation and Characterisation of TiO₂ Produced from Sludge After Flocculation

The mechanism of TiO₂ 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. TiCl₄ changes to TiOCl₂ in an aqueous phase and the TiOCl₂ 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 TiOₓ·yCₜₜₙₙPₓ₁₄ (obtained from X-ray photoelectron spectroscopy analysis).

The crystallite size of the TiO₂ produced from the sludge after incineration of 600 °C with synthetic wastewater was 6.0 nm (Figure 5).
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 TiO₂ was 76.3 m²/g, which was higher than that of TiO₂-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 TiO₂. These atoms help the improvement of TiO₂ photoactivity. The atomic percentage of Ti, O, C and P of the TiO₂ was 26.9 : 51.5 : 15.8 : 5.8[5]. The photocatalytic property of the TiO₂ was investigated for the photodecomposition of gaseous acetaldehyde and was then compared to that of the TiO₂-P25 photocatalyst (Figure 6). The functional TiO₂ was better in all aspects than the commercially available TiO₂-P25 and up to 20% better for the removal of acetaldehyde than the TiO₂-P25 under UV irradiation. After 90 minutes of the photocatalytic reaction, the functional TiO₂ 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 TiO₂ thermal catalyst. This suggests that the TiO₂ produced from sludge during incineration also led to preferential removal of PCDFs.
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 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 produced from incineration of the settled floc at 600 °C (A: anatase phase (TiO₂); H: hematite (α-Fe₂O₃)).
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).

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

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

<table>
<thead>
<tr>
<th></th>
<th>Crystallite size (nm)</th>
<th>Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DW</td>
<td>13</td>
<td>90.2</td>
</tr>
<tr>
<td>WW</td>
<td>15</td>
<td>103.5</td>
</tr>
<tr>
<td>SW</td>
<td>40</td>
<td>68.1</td>
</tr>
<tr>
<td>P-25</td>
<td>25</td>
<td>42.3</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th></th>
<th>Atomic %</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>DW</td>
<td>3.87</td>
<td>65.92</td>
</tr>
<tr>
<td>WW</td>
<td>4.82</td>
<td>59.58</td>
</tr>
<tr>
<td>SW</td>
<td>4.62</td>
<td>67.08</td>
</tr>
</tbody>
</table>

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 photodecomposition 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 removal 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 photocatalytic activity 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,
WW, SW and TiO$_2$-P25 was 90.2, 103.5, 68.1 and 42.3 m$^2$/g, respectively.

TiO$_2$ 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 TiO$_2$ depend on water characteristics from different water sources.

7. Effect of Washing TiO$_2$ Prepared from Ti-salts Flocculated Wastewater Sludge

Due to the TiO$_2$ production from different water sources present in many different organic/inorganic compounds, it is important to investigate the washing effect of TiO$_2$ produced from sludge. El Saliby et al.[16] examined the effect of washing on TiO$_2$ produced from sludge of Ti-salt flocculation with synthetic wastewater. The TiO$_2$ 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 TiO$_2$ after different washings showed several benefits. Washed TiO$_2$ improved the adsorption and the photocatalytic ability in decomposing acetaldehyde under UV-irradiation. TiO$_2$ after basic washing was fast in decomposing organic compounds in water phase in terms of organic removal. Similarly, TiO$_2$ after acidic washing was better than as-prepared TiO$_2$.

8. Verification of a Pilot-scale Ti-salt Flocculation to Produce TiO$_2$ 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 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 m$^3$/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 m$^3$/h. The dewatered sludge was dried in rotary furnace at 300 °C. The dry sludge was incinerated at 600 °C to remove organic content of the sludge.

XRD patterns were drawn to identify the structure of TiO$_2$ from dye wastewater (TiO$_2$-DWW). Sludge generated from the flocculation of DWW using TiCl$_4$ was incinerated at 600 °C to produce TiO$_2$-DWW. XRD results showed that the anatase structure was predominant in TiO$_2$-DWW. Transmission electron microscopy image showed that 15 ~20 nm anatase particles are present after incineration at a temperature of 600 °C (Figure 11). Table 3 shows SEM/EDX results for TiO$_2$-DWW. TiO$_2$-DWW was mainly doped with carbon atoms. Many
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 TiO$_2$-DWW. TiO$_2$-P25 was used as a commercial TiO$_2$ reference for assessing the results obtained from TiO$_2$-DWW. Acetaldehyde was adsorbed onto TiO$_2$-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 TiO$_2$-DWW and TiO$_2$-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 TiO$_2$-DWW and TiO$_2$-P25 in terms of photocatalytic oxidation of acetaldehyde, which indicates the potential use of TiO$_2$-DWW for decomposing volatile organic contaminants.

### Table 3. Atomic fraction of TiO$_2$-DWW and TiO$_2$-P25

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic% of TiO$_2$-DWW after TiCl$_4$ flocculation</th>
<th>Atomic% of TiO$_2$-P25</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>5.09</td>
<td>-</td>
</tr>
<tr>
<td>O</td>
<td>62.80</td>
<td>76.98</td>
</tr>
<tr>
<td>Na</td>
<td>0.56</td>
<td>-</td>
</tr>
<tr>
<td>Si</td>
<td>1.12</td>
<td>-</td>
</tr>
<tr>
<td>Ti</td>
<td>30.20</td>
<td>23.02</td>
</tr>
<tr>
<td>etc</td>
<td>0.23</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

9. Hydrogen Production from TiO$_2$ 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 TiO$_2$ as catalyst[21,23,24]. Presently, the energy conversion efficiency from solar to hydrogen by TiO$_2$ photocatalytic water-splitting is still low, mainly due to: 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 TiO$_2$ 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 H$_2$ and O$_2$ to form H$_2$O is thermodynamically favourable. Therefore, the addition of sacrificial electron donor (organic compounds) which becomes progressively oxidized toward CO$_2$ 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 H$_2$ production was achieved with the addition of methanol to the suspension. Similarly, the production of H$_2$ via methanol/water photodecomposition was enhanced with Cu/TiO$_2$ compared to TiO$_2$[31]. The production of H$_2$ reached 13500 µmol after methanol/water photodecomposition for 10 h over 10% mol Cu/TiO$_2$ 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/TiO$_2$ 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 TiO$_2$-DWW which was produced from the incineration of dye wastewater flocculated sludge to produce H$_2$ energy. They doped TiO$_2$-DWW with Pt metal to increase H$_2$ production. Figure 12 shows the variation of H$_2$ production by photocatalytic reforming of methanol (6 vol%).

10. Aquatic Toxicity Evaluation of TiO$_2$ Nanoparticle Produced from Sludge of TiCl$_4$ 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 TiO$_2$ nanoparticles. However, the toxicity of Ti-salt is not known to be safely used in water treatment. Aquatic tox-
The aquatic toxicity, *D. magna* mortality, of TiO$_2$ produced from different wastewater sources was investigated by Lee et al.\[15\]. TiO$_2$ concentration varied from 0 mg/L to 200 mg/L. The maximum mortality of TiO$_2$ produced from SWW, WW, and SW was less than 15%, while that of TiO$_2$-P25 was 25% at the concentration of 100 mg/L. As all the TiO$_2$ 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 TiO$_2$ showed lower values of LC5 (5.9 mg/L), LC10 (28.4 mg/L), and LC15 (81.3 mg/L) compared to TiO$_2$ produced from SWW, WW, and SW. This result clearly indicates that TiO$_2$ nanoparticles produced from SWW, WW, and SW have low acute toxicity in aqueous conditions. This is in good agreement with the previous studies\[36,37\]. Johnson et al.\[36\] reported that mean concentration values of TiO$_2$ required to immobilize 50% of *D. magna* was more than 1 g/L. Lovern and Klaper\[37\] found that mortality with sonicated TiO$_2$ was less than 9% and the LC50 was zero for the sonicated TiO$_2$ solution. However, when exposed to the filtered TiO$_2$ 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 TiO$_2$ 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, FeCl$_3$, and Al$_2$(SO$_4$)$_3$ 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 °C produced a useful byproduct (TiO$_2$). In another study, drinking water, seawater, and wastewater flocculation was investigated to produce different types of TiO$_2$. In general, TiO$_2$ from different water sources was mainly doped with 3~5% carbon atoms, while TiO$_2$ produced from synthetic wastewater was doped with C and P atoms to up to 20%. Anatase structure was predominant for all TiO$_2$.
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 easier 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

This review was supported by CRC-CARE, the Korea Research Foundation Grant funded by the Korean Government (KRF-2007-412-J02002) and the Center for Photonic Materials and Devices at Chonnam National University.

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