Preparation and characterisation of titanium dioxide (TiO$_2$) produced from Ti-salt flocculated sludge in water treatment

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Abstract
During the past few years, titanium salts were investigated as alternative coagulants for the removal of organic matter of different molecular sizes from contaminated water. Ti-salt flocculation efficiency was comparable to FeCl$_3$ and Al$_2$(SO$_4$)$_3$ salts with an additional benefit which relies in the production of TiO$_2$ from the incineration of the settled floc. Sludge-TiO$_2$ showed higher surface area and photocatalytic activity than commercially available TiO$_2$. Metal-doped forms were produced by a simple addition of coagulant aids such as iron (Fe-), aluminium (Al-) and (Ca-) calcium salts during Ti-salt flocculation to increase pH and to produce Fe-, Al- and Ca-doped TiO$_2$. Ca- and Al- doped TiO$_2$ showed very high photocatalytic activity compared with Fe-doped TiO$_2$. On the other hand, a pilot scale plant study was conducted to demonstrate the feasibility of the novel process using TiCl$_4$ flocculation with dye wastewater. The removal ratio of the chemical oxygen demand was comparable to the commonly used coagulants while the settling of sludge was faster which made the subsequent separation process easier. The TiO$_2$ generated after sludge incineration had a high photocatalytic degradation of volatile organic compounds and has increased the rate of hydrogen production from water photosplitting. Aquatic toxicity of TiCl$_4$ coagulant and TiO$_2$ produced from different water sources with different concentrations using *D. magna* mortality showed low acute toxicity effect compared with known heavy metals and commercial TiO$_2$. This paper presents the production, characterisation and the photoactivity of TiO$_2$ produced from Ti-salt flocculated sludge. Different case studies are discussed to highlight recent advances in this field.

Keywords: flocculation, titanium salts, flocculated sludge, incineration, TiO$_2$, photocatalysis, hydrogen production

1. Introduction

1.1. Flocculation for treating 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, wastewater treatment was continually 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. 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 removing organic matter, which causes trihalomethane formation 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 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. Thus, a chemical (coagulant) that produces less sludge or reusable material can offer environmental and economical benefits associated with sludge handling.

1.2. Application of TiO_2

TiO_2 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. Photoinduced electrons (e^-) and positive holes (h^+) are produced from TiO_2 with UV light. These charged species can further generate free radicals. The highly oxidising positive hole (h^+) is considered to be the dominant oxidising species in the mineralisation process. The usefulness of TiO_2 for degrading contaminants in many applications means the demand for TiO_2 is greatly increasing. Generally, TiO_2 used for industrial applications is produced using 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 used to produce TiO_2 discharge a large amount of wastewater which contains strong acid and chloride/sulfate ions at high concentrations, which results in difficulty of wastewater treatment without cost-intensive advanced processes.

1.3. Objectives

To resolve the above problems, a new solution to the sludge problem through a process which recovered economically valuable TiO_2 from synthetic wastewater (SWW) has been developed [5]. A large amount of functional TiO_2 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 the benefits of the processes is shown in Figure 1. This review aimed to investigate the past, present and future experience and knowledge of the preparation of TiO_2 produced from Ti-salt flocculated sludge.
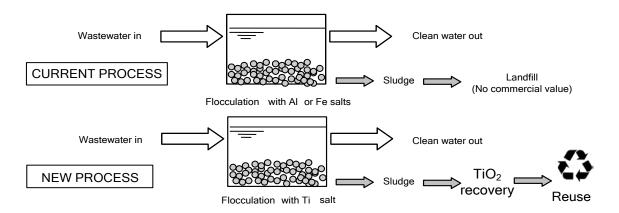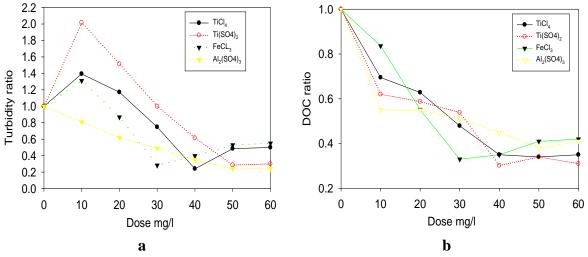
Figure 1. Comparison of the new process described in this review with conventional flocculation

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 titanium sulfate ($Ti(SO_4)_2$) was better in fluoride removal due to a quadrivalent cation instead of the trivalent aluminium or iron ion. They added that ilmenite extract gave much better coagulation in the coloured water high in colloidal matter and dissolved salts than aluminium or ferric sulfates. Furthermore, titanium salts appeared 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 Ti salts flocculation. Wastewater can be efficiently purified to remove fluoride ions with titanium (IV) compounds, especially with hydrated oxotitanium sulfate with [F⁻] concentration achieved of 0.5-0.6 mg/l. They found that the concentration of the sulfate ions in 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 that 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 were 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, 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. 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 $FeCl_3$ compared with $Al_2(SO_4)_3$. It can be concluded that Ti-salt coagulants have a high potential to apply for 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 using $FeSO_4$ as coagulant, while $TiCl_4$ degraded 75.9%

of COD_{Mn}. On the other hand, the precipitation efficiency was better for $TiCl_4$ compared with $FeSO_4$.

a   b

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

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, which has a significant potential to the lower cost of waste disposal, protect the environment and public health and yield economically useful by-products [10]. Figure 3 shows XRD images to identify the particle crystalline structure after calcination of the settled floc at different temperatures from 100 to 1000 ºC. After $TiCl_4$ flocculation, the anatase pattern was found from more than 600 °C (Figure 2a). At lower temperature, remaining organic matter interfered TiO_2 production. At 1000 °C, 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 °C 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 a way are efficient and economical not only in terms of removal of organic matter in wastewater, but also in sludge reduction. As the metal oxides can be produced in significant quantities in 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.
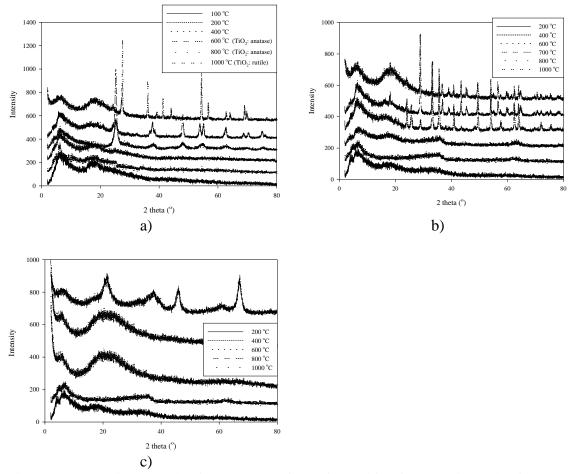
Figure 3. XRD images a) of the settled floc after TiCl₄ flocculation, b) of the settled floc after FeCl₃ flocculation and c) of the settled floc after Al₂(SO₄)₃ flocculation by calcination at different temperatures

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 fully explained because flocculation is a very complex phenomenon, which is not clearly proven. However, it can be generally explained as shown in Figure 4. As coagulant, $TiCl_4$ changes into $TiOCl_2$ when it is placed in aqueous phase. Depending on the pH of the system, the $TiOCl_2$ hydrolyses to $Ti(OH)_4$. The 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 a compound of $TiO_{1.42}C_{0.44}P_{0.14}$ (obtained from X-ray photoelectron spectroscopy analysis).
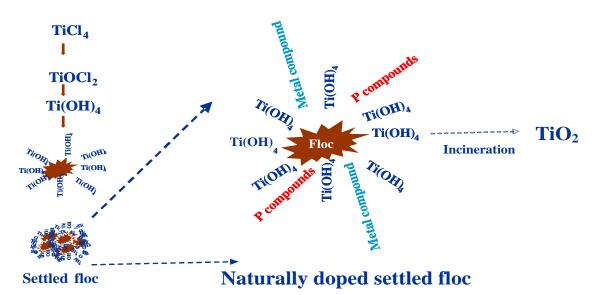
Figure 4. Mechanism of the floc formation by TiCl₄ flocculation and TiO₂ production

The crystallite size of the TiO_2 produced from sludge after incineration of 600 °C with synthetic wastewater was 6.0 nm (Figure 5). The specific surface area of the functional TiO_2 was 76.3 m^2/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 in improving 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 was up to 20% better at removing acetaldehyde than the TiO_2-P25 under UV irradiation. After 90 minutes of photocatalytic reaction, the functional TiO_2 photocatalysis removed the majority of acetaldehyde. Further during incineration of wastewater residues, dioxin-like polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzo-furans (PCDFs) present in the residue pose health hazards. To investigate the formation and decomposition of PCDD/Fs and dioxin-like PCBs during incineration of flocculated sludge, the concentrations of PCDD/Fs and dioxin-like PCBs were measured in the residues. The removals of PCDDs, PCDFs and dioxin-like PCBs were 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.
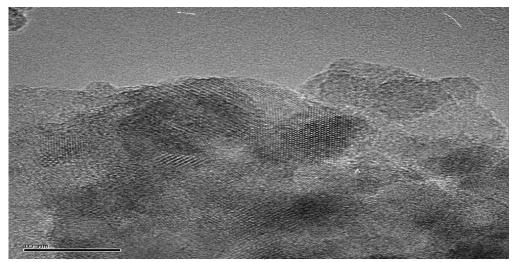
Figure 5. High resolution transmission electron microscope image of TiO$_2$ produced from sludge with Ti-salt flocculation

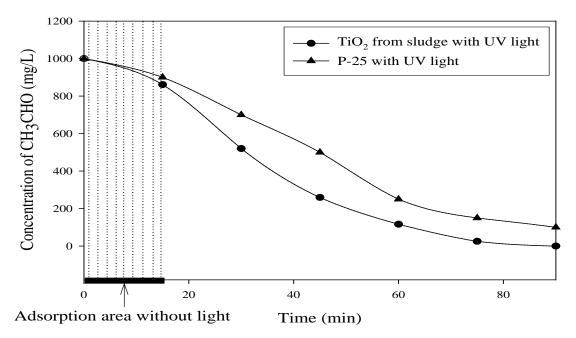Adsorption area without light   Time (min)

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 TiO$_2$ from sludge produced by TiCl$_4$ flocculation with FeCl$_3$, Al$_2$ (SO$_4$)$_3$ 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 TiCl$_4$ 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 TiCl$_4$ flocculation. The post-treatment would be an addition of sodium hydroxide (NaOH) to neutralize the pH value. Alternatively, coagulant aids such as FeCl$_3$, Al$_2$(SO$_4$)$_3$ and Ca(OH)$_2$ could be simultaneously added during flocculation with TiCl$_4$. Incineration of co-flocculated sludge would produce Fe-, Al- and Ca-doped TiO$_2$.

Shon et al. [10] studied on increasing the pH after Ti-salt flocculation together with Fe-salt, Al-salt and Ca-salt flocculation. They also investigated the variation of TiO_2 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 the increase in concentration of the 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.

TiO_2 without any coagulant aids is called as TiO_2-WO. TiO_2 obtained from $TiCl_4$ coagulant together with Fe-, Al- and Ca-salt coagulant aids at the different optimum concentrations are expressed as Fe/TiO_2, Al/TiO_2 and Ca/TiO_2, respectively. Figure 7 presents the XRD patterns of TiO_2-WO, Fe/TiO_2, Al/TiO_2 and Ca/TiO_2 incinerated at 600 ℃. The TiO_2-WO, Fe/TiO_2, Al/TiO_2 and Ca/TiO_2 exhibited the majority of the anatase phase. The XRD pattern on the Fe/TiO_2 showed a peak of hematite (α-Fe_2O_3). The peak of low intensity, due to an iron-TiO_2 mixed phase, of composition Fe_2TiO_5, crystallized poorly in very small grain sizes evidenced by the remarkable enlargement of the diffraction peak, as detected on the Fe/TiO_2. A crystalline phase containing Al atoms (α-Al_2O_3 and Al_2TiO_5) was not observed in the Al/TiO_2. This is due to low concentrations of Al_2O_3 and/or a substitute site (Al^{3+}) for a Ti^{4+} ion. Since the ionic radius for Al and Ti are similar (0.68 Å for Al^{3+}), Al can occupy a regular cation position, forming a substitutional solid solution. In addition, Al species dissolve well into the TiO_2 crystal. The crystalline phase containing Ca atoms (CaO and $CaTiO_3$) was not observed on the Ca/TiO_2. To sum up, different crystalline phases such as α-Al_2O_3 and Al_2TiO_5 from Al/TiO_2 and CaO and $CaTiO_3$ from Ca/TiO_2 were not found. On the other hand, the XRD pattern of α-Fe_2O_3 from Fe/TiO_2 was observed. The crystalline size of different TiO_2 was calculated using Scherrer's formula [11]. The crystallite size of TiO_2-WO, Fe/TiO_2, Al/TiO_2 and Ca/TiO_2 was approximately 11 nm, 6 nm, 8 nm and 11 nm, respectively. The intensity of the anatase phase on Fe/TiO_2 and Al/TiO_2 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/TiO_2 was similar to that on the TiO_2-WO.
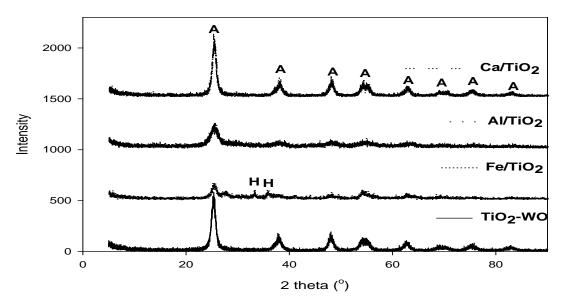
Figure 7. XRD patterns of TiO$_2$-WO, Fe/TiO$_2$, Al/TiO$_2$ and Ca/TiO$_2$ produced from incineration of the settled floc at 600 ºC (A: anatase phase (TiO$_2$); H: hematite (α-Fe$_2$O$_3$))

The photocatalytic property of TiO$_2$-WO, Fe/TiO$_2$, Al/TiO$_2$ and Ca/TiO$_2$ was examined under irradiation of UV and visible light for the photodecomposition of gaseous acetaldehyde (Figure 8). TiO$_2$-P25 was used to compare the photocatalytic activity with other TiO$_2$. The concentration of acetaldehyde was measured by gas chromatography. The removal by adsorption showed the following order: Al/TiO$_2$ (136 m^2/g) >> Ca/TiO$_2$ (116 m^2/g) > TiO$_2$ (122 m^2/g) > Fe/TiO$_2$ (77 m^2/g) ≥ TiO$_2$-P25 (50 m^2/g). The majority of acetaldehyde with TiO$_2$-WO and Ca/TiO$_2$ was completely removed under UV irradiation within 40 minutes. TiO$_2$-P25 and Al/TiO$_2$ 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 Fe$_2$O$_3$ and Fe$_2$TiO$_5$ at high incineration temperature (600 ºC - 800 ºC) 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 TiO$_2$-WO, Fe/TiO$_2$, Al/TiO$_2$, Ca/TiO$_2$ and TiO$_2$-P25 was marginal.
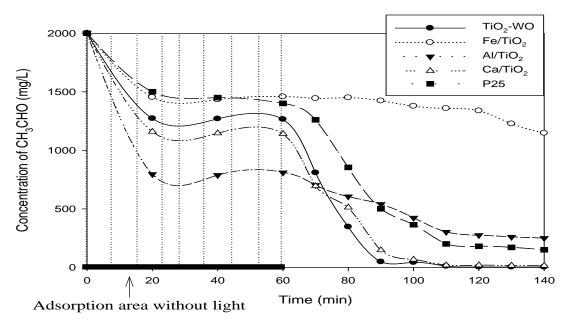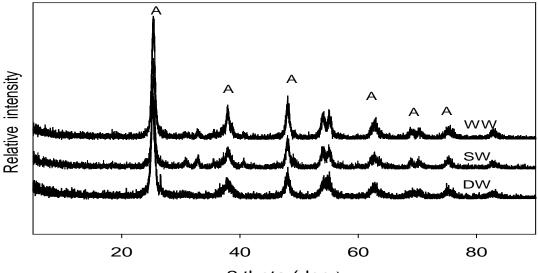
Figure 8. Variation of acetaldehyde concentration with UV irradiation time (TiO$_2$ concentration = 1 g; initial concentration = 2000 mg/L; UV irradiation = black light three 10 W lamps)

6. TiO$_2$ 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 TiO$_2$ 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.

Figure 9. XRD patterns of TiO$_2$ produced from DW, WW and SW sources

Table 1 shows the characteristics of TiO_2 produced from DW, WW and SW in terms of crystallite size and BET surface area and TiO_2 was compared with P25. The crystallite size of TiO_2 from DW, WW, SW and TiO_2-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 TiO_2 nanoparticles from DW, WW, SW and TiO_2-P25 was 90.2, 103.5, 68.1 and 42.3 m^2/g, respectively.

Table 1. Crystallite size and BET surface area of TiO_2 produced from different water sources

TiO_2	Crystallite size (nm)	Surface area (m^2/g)
DW	13	90.2
WW	15	103.5
SW	40	68.1
P-25	25	42.3

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.

Table 2. EDX results of TiO_2 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

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.
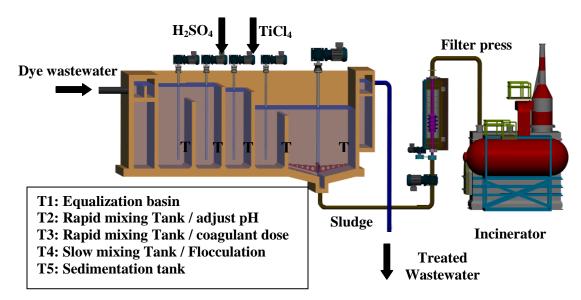

Figure 10. Schematic diagram of the pilot-scale flocculation basin to produce TiO$_2$ from sludge with DWW

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

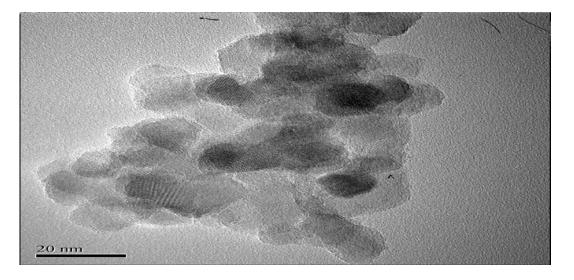acetaldehyde, which indicates the potential use of TiO$_2$-DWW for decomposing volatile organic contaminants.

Figure 11. High-resolution transmission electron microscope image of TiO$_2$-DWW

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

Element	Atomic% of TiO$_2$-DWW after TiCl$_4$ flocculation	Atomic% of TiO$_2$-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

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, 18, 19, 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 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 TiO$_2$ surface [26, 27, 28, 29 ,30] or the use of organic solvents as "sacrificial reagents" [27, 29,31, 32, 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_2O 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 hrs 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 in relation to Pt deposition concentration on TiO_2-DWW. To prevent the recombination, TiO_2 produced from sludge was doped with Pt metal to hold electrons. These Pt-deposited TiO_2 nanoparticles were placed in the photoreactor containing pure water and methanol. As the doping concentration of Pt deposited on TiO_2 produced from DWW sludge increased from 0.01% to 0.5%, the H_2 amount increased. The H_2 amount with 0.5% Pt/TiO_2 was 10201 µmol. The increase in H_2 production rate in relation to the increased Pt deposition on TiO_2 may be due to effective loading of the co-catalyst (Pt) on the catalyst (TiO_2) and the formation of increased Schottky barriers (potential barrier formed at a metal-TiO_2 junction which has rectifying characteristics) between Pt and TiO_2 [33].
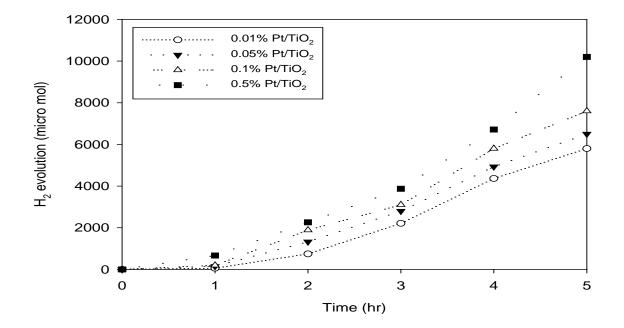
Figure 12. Effect of Pt deposition concentration on DWT for H$_2$ production by photocatalytic reforming of methanol (6 vol%).

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 toxicity of the TiCl$_4$ 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 TiCl$_4$ flocculation and recovered TiO$_2$ nanoparticles from the sludge.

Aquatic toxicity of TiCl$_4$ coagulant was investigated using *D. magna* mortality with different TiCl$_4$ concentrations (Figure 13). TiCl$_4$ ranging from 0 mg/L to 200 mg/L concentration was exposed to *D. magna*. The exposure with TiCl$_4$ concentration of less than 80 mg/L experienced no fatalities. However, TiCl$_4$ concentrations of 100 mg/L exhibited 15%, and 150 mg/L and 200 mg/L both exhibited 25% mortality. Median lethal concentration of TiCl$_4$ was investigated in terms of LC5, LC10, LC15 and LC50. The LC5, LC10, LC15 and LC50 of TiCl$_4$ 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 TiCl$_4$ exhibited higher concentration. This means that TiCl$_4$ coagulant has low acute toxicity in water compared to above mention heavy metals.
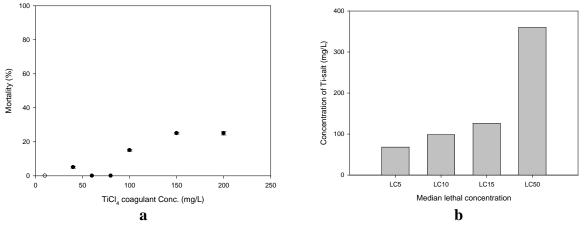

a   b

Figure 13. (a) Mortality of *D. magna* on exposure to TiCl$_4$ coagulant and (b) median lethal concentration of TiCl$_4$

The aquatic toxicity, *D. magna* mortality, of TiO$_2$ produced from different waster sources was investigated by Lee et al. [15]. TiO$_2$ concentration was varied from 0 mg/L to 200 mg/L. The maximum mortality of TiO$_2$ produced from SWW, WW from biologically treated sewage effluent 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 condition. 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.
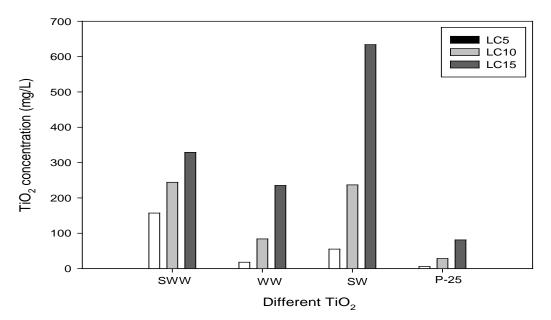

Figure 14. Concentration values of LC5, LC10 and LC15 to TiO_2 produced from SWW, WW and SW

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 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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