

# Magnetised Titanium Dioxide (TiO<sub>2</sub>) for Water Purification: Preparation, Characterisation, and Application

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## Abstract

The study of titanium dioxide (TiO<sub>2</sub>) as a photocatalyst for water purification has attracted significant attention over the past four decades. However, the separation of photocatalyst from water suspension may be difficult, costly and jeopardize the use of this water treatment technology. Recently, the development and production of magnetised TiO<sub>2</sub> have been achieved to offer a solution for the photocatalyst separation problem. This paper discusses the preparation techniques, characterisation and the applications of magnetised TiO<sub>2</sub>. Many researchers have studied magnetised TiO<sub>2</sub> photocatalysts but the lack of articles discussing the water purification processes is still slowing any advance in this field. Here, the progress of the scientific research on preparation techniques to coat magnetic particles by materials such as organic polymers, silica, magnesia and alumina are reviewed to compare and discuss recent findings. The doping of photoactive TiO<sub>2</sub> photocatalyst into the magnetic coated particles is also emphasised. In addition, the characterisation of magnetised TiO<sub>2</sub> in terms of physicochemical properties and operating conditions produced by each technique are critically reviewed. Moreover, examples of applications of TiO<sub>2</sub> and magnetised TiO<sub>2</sub> photocatalyst in water purification are summarised. In general, the effectiveness of organic removal by magnetised TiO<sub>2</sub> is still lower compared to single phase TiO<sub>2</sub>. The future prospect of this field is deliberated to develop a novel, economic and efficient magnetised TiO<sub>2</sub> photocatalyst, which has high organic removal properties.

**Keywords:** Photocatalyst, Purification, Characterization, Magnetised TiO<sub>2</sub>.

## 1. Introduction

Clean water resources are essential for the existence of life. Over one billion people throughout the world have no safe drinking water, and almost two and a half billion people do not have access to adequate sanitation. To provide people with water and ease the strain on deteriorating supplies of freshwater, recycled water has been touted as a solution. Nowadays, many conventional technologies such as membrane filtration (microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO)) and/or advanced oxidation processes (AOP) heterogeneous photocatalyst were widely used to remove undesirable natural organic matter (NOM) from natural and wastewater (Herrmann 1999; Parsons 2004; Tansel 2008a; Tansel 2008b). In terms of waste disposal and possibility of further treatment, AOP heterogeneous photocatalyst offered more advantageous over membrane filtration due to rapid conversion reaction, such as mineralising the hazardous contaminants to harmless compound such as carbon dioxide ( $\text{CO}_2$ ), water ( $\text{H}_2\text{O}$ ), simple acids and salts, therefore, it does not generate waste streams and disposal problems. In addition, AOP treatment promises to utilise sunlight as an ample and clean energy resource to reduce the environmental pollution, and uses ambient oxygen rather than expensive oxidants such as hydrogen peroxide and ozone (Andreozzi et al. 1999).

In photocatalytic oxidation (PCO), a semiconductor photocatalyst is illuminated by light of a suitable wavelength to generate hydroxyl radicals that are able to initiate a chain of redox reactions to degrade organic pollutants. The most effective photocatalyst for widespread environmental application is titanium dioxide. It is stable, non-toxic, biologically and chemically inert and inexpensive. The principle of photocatalytic oxidation is described in Figure 1.

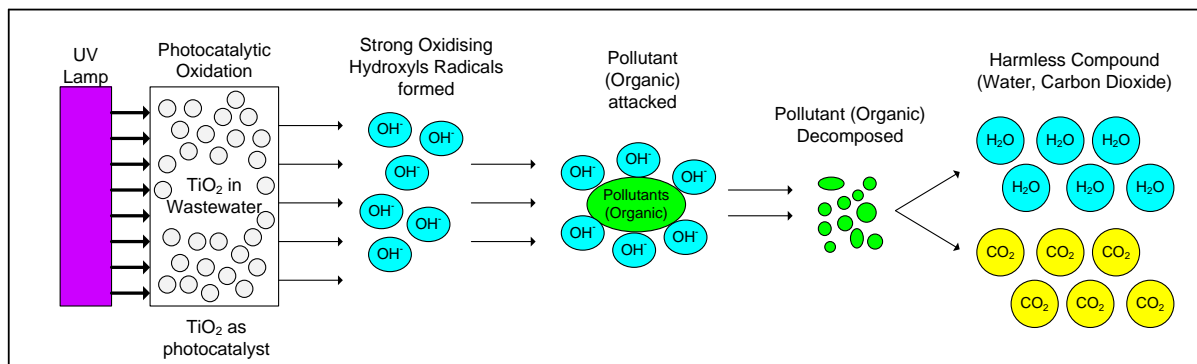


Figure 1: The Principle of Photocatalytic Oxidation Process.

In order to fully appreciate the characteristics of photocatalysis with this semiconductor, it is necessary to understand the basic physics of semiconductor materials. The titania catalyst is illuminated by UV radiation with a wavelength sufficient to displace electrons from the valence band of the catalyst; for titanium dioxide this is below 387.5nm. When photocatalyst titanium dioxide ( $\text{TiO}_2$ ) absorbs ultraviolet (UV) radiation, an electron/hole pair is produced on the semiconductor surface. Thus produced photo induced electrons ( $e^-$ ) and positive holes ( $h^+$ ) further generate hydroxyl and oxygen free radicals. The photocatalytic oxidation of an organic species often proceeds via adsorption of the pollutant on the surface of the catalyst, followed by direct subtraction of the pollutant's electrons by positively charged holes. Another possible way is oxidation with OH radicals, generated from water of the aqueous

environment, which takes place at the catalyst surface or in its vicinity. Both reactions may proceed simultaneously and which mechanism dominates depends on the chemical and adsorption properties of the pollutant. In the literatures, the semiconductor, titanium dioxide (TiO<sub>2</sub>) is the most thoroughly investigated due to its excellent properties and also has attracted significant attention over the past four decades (Chen et al. 2010; Fujishima & Honda 1972; Howe 1998; McCullagh et al. 2007; Tung & Daoud 2009; Watson et al. 2005; Xuan et al. 2009).

In terms of reactor configuration system, there are two typical systems used in water purification applications namely, slurry-type reactor where the catalyst particles are fully integrated in the liquid mobile phase and immobilised-type reactor where the catalyst particles are immobilised or attached onto the fixed support. Many studies proved that slurry-type reactors are much more efficient than immobilised-catalyst type reactor (Beydoun et al. 2000; Beydoun et al. 2001; de Lassa, Serrano & Salaices 2005; Geissen et al. 2001). The comparisons between photocatalytic slurry-type reactors and immobilised-type reactors are described in Table 1.

Table 1: Comparison of photocatalytic slurry-type and immobilised-type reactors

Note: Adopted from (de Lassa, Serrano & Salaices 2005)

	<b>Slurry-Type Reactors</b>	<b>Immobilised-Type Reactors</b>
<b>Advantages</b>	<ul style="list-style-type: none"> <li>- Fairly uniform catalyst distribution</li> <li>- High photocatalytic surface area to reactor volume ratio</li> <li>- Limited mass transfer</li> <li>- Minimum catalyst fouling effects due to the possible continuous removal and catalyst replacement</li> <li>- Well mixed particle suspension</li> <li>- Low pressure drop through the reactor</li> </ul>	<ul style="list-style-type: none"> <li>- Continuous operation</li> <li>- Improved removal of organic material from water phase while using a support with adsorption properties</li> <li>- No need for an additional catalyst separation operation</li> </ul>
<b>Disadvantages</b>	<ul style="list-style-type: none"> <li>- Requires post – process filtration</li> <li>- Important light scattering and adsorption in the particle suspended medium</li> <li>- Difficulty to recover the fine photocatalyst particles from treated effluent</li> </ul>	<ul style="list-style-type: none"> <li>- Low light utilisation efficiencies due to light scattering by immobilised photocatalyst</li> <li>- Restricted processing capacities due to possible mass transfer limitations</li> <li>- Possible catalyst deactivation and catalyst wash out</li> </ul>

In water and wastewater purification applications, photocatalytic reaction with TiO<sub>2</sub> can either be carried out in a slurry system or immobilised system. Despite of its great properties it seems that TiO<sub>2</sub> may cause difficulties during the separation phase from water.

Although the slurry-type reactor was effective, it requires post-process separation stage, additional chemicals required, and it is difficult to recover the fine photocatalyst particles from the treated effluent, which limits the potential use of TiO<sub>2</sub> on a commercial scale (de Lassa, Serrano & Salaices 2005; Watson et al. 2005). There are one approach to overcome this separation problem by developing a stable magnetic photocatalyst which allows for easy remaining recovery by the use of external magnetic field and thus, it increases the reusability of the photocatalyst. There are many studies on the preparation of magnetic photocatalyst, however, this paper is the first to review the field with a focus on water purification.

An overview of magnetised TiO<sub>2</sub> and its preparation techniques to coat magnetic materials is compared and discussed. The doping of photoactive TiO<sub>2</sub> photocatalyst into the coated magnetic materials is also emphasized. The characterisation of magnetised TiO<sub>2</sub> in terms of physicochemical properties and operating conditions produced by each technique are critically reviewed. Examples of applications of TiO<sub>2</sub> and magnetised TiO<sub>2</sub> photocatalyst in water purification are summarised.

## **2. Magnetised TiO<sub>2</sub>**

The semiconductor, TiO<sub>2</sub> is certainly the most common and promising material used as a photocatalyst in purification technologies nowadays. Highly photoactive, inexpensive and chemically stable are the most important properties of TiO<sub>2</sub> (Tryk, Fujishima & Honda 2000). According to Hoffmann (1995), TiO<sub>2</sub> is used as an answer to environmental problems. For instance, it has been used to remove undesirable organic contaminants which dissolved in air and water. Additionally, in focus of water treatment, TiO<sub>2</sub> has been mainly used in the form of suspension or in the form of thin film (Beydoun et al. 2000; Chang, Wu & Zhu 2000; Chen & Zhao 1999; Gad-Allah et al. 2009; Hurum et al. 2003; Kwon et al. 2008; Luo, Bowden & Brimblecombe 2009; Noorjahan et al. 2003; Rashed & El-Amin 2007; Samarghandi et al. 2007; Theron et al. 2001; Watson, Beydoun & Amal 2002; Zainudin, Abdullah & Mohamed 2008).

There are two most common crystalline forms of TiO<sub>2</sub> which are used as photocatalyst, namely, rutile and anatase forms. Degussa P-25 is an example for commercially available TiO<sub>2</sub> photocatalyst which compositions are approximately consisting of 25% rutile and 75% anatase form (Ohno et al. 2001). It has been used as a standard for photocatalytic degradation application in many studies (Swetha, Santhosh & Balakrishna 2010). Moreover, TiO<sub>2</sub> anatase form was the most widely used photocatalyst and proves to be more efficient, due to its higher surface area and open structure compared to rutile form (Al-Rasheed 2005; Bacsa & Kiwi 1998). However, this form only can utilise only UV irradiation due to its relatively high 3.2 eV band gap. Therefore, intensive studies have been carried out to develop a solar light sensitive photocatalysts by using doping techniques to reduce the semiconductor band gap to solar light irradiation region. It has been widely reported in the literature, for example using doping with nitrogen (Sato 1986), carbon (Ohno et al. 2001; Ren et al. 2007), iron (Tryba 2008) and sulphur (Abbas J. Attia 2008; Ohno et al. 2004). Photocatalysts doped with noble metals and metals (Siemon et al., 2002; Vamathevan et al., 2004) show improved efficiency in the destruction of various compounds, compared to TiO<sub>2</sub> particles alone.

Although,  $\text{TiO}_2$  is very effective in removing organic contaminants from treated effluent, it also causes difficulties during the separation phase from water due to the small particle size (nanoparticle). Therefore, one approach is to develop a stable magnetic photocatalyst for easy recovery by applying external magnetic field. The development of magnetic photocatalyst for environmental remediation has been numerously reported in literatures (Beydoun 2000; Beydoun & Amal 2002; Beydoun et al. 2001; Bruce et al. 2004; Buske 1994; Chambers, Droubay & Kaspar 2006; Chen, Deng & Zhang 2010; Chen et al. 2009a; Chen et al. 2009b; Chen et al. 2009c; Fukumura, Toyosaki & Yamada 2005; Gad-Allah et al. 2008; Gad-Allah et al. 2009; Hai 2009; He et al. 2008; Li et al. 2009; Nunes et al. 2006; Philipse, van Bruggen & Pathmamanoharan 1994; Tural, Ozkan & Volkan 2009; Watson, Beydoun & Amal 2002; Watson et al. 2005; Wen et al. 2009; Xu, Bao & Zhang 2005; Xu et al. 2007; Xu et al. 2008; Xuan et al. 2009; Zhang, Zhang & Feng 2008). Various magnetic cores had been used to develop magnetic  $\text{TiO}_2$  which is summarized in Table 2.

Table 2: Various Magnetic Cores used to Develop Magnetised TiO<sub>2</sub>

<b>Magnetic Photocatalyst Cores Type</b>	<b>Examples</b>	<b>Finding(s)</b>	<b>Reference(s)</b>
Iron Oxides	<ul style="list-style-type: none"> <li>- Magnetite (Fe<sub>3</sub>O<sub>4</sub>)</li> <li>- Maghemite (γ-Fe<sub>2</sub>O<sub>3</sub>)</li> </ul>	<ul style="list-style-type: none"> <li>- This photocatalyst was synthesized by coating titanium dioxide particles onto colloidal magnetite and nano-magnetite particle. This study explained in terms of the stability of magnetite phases present and photodissolution effect on magnetite by TiO<sub>2</sub>. The intermediate silica coating to prevent the photodissolution was also clearly described. This composite nanoparticles also used to degrade sucrose under UV illumination</li> <li>- This photocatalyst can photodegrade organic pollutants in the dispersion system effectively and can be recycled easily by a magnetic field. The sample activity sintered at 500°C showed the highest activity for the degradation of aqueous solution of acridine dye.</li> </ul>	<p>(Beydoun 2000; Watson et al. 2005)</p> <p>(Gao et al. 2003)</p>
Metal Ferrites	<ul style="list-style-type: none"> <li>- Nickel ferrite</li> <li>- Cobalt ferrite</li> <li>- Strontium ferrite</li> </ul>	<ul style="list-style-type: none"> <li>- This photocatalyst was prepared using continuous multi-step pyrolysis process. It has been used to photodegrade methylene blue (MB) for about 90 minutes per cycle. It has been found out that the photoactivity of the composite nanoparticle remained unchanged after magnetic separation and washing.</li> <li>- A magnetically separable photocatalyst TiO<sub>2</sub>/SiO<sub>2</sub>/NiFe<sub>2</sub>O<sub>4</sub> (TSN) was prepared by a liquid catalytic phase transfer method and it is also easily redispersed in treated water. Moreover, it has been used to degrade methyl orange in water. This magnetic photocatalyst demonstrated a good repeatability of the photocatalytic activity after several recycled.</li> <li>- This photocatalyst was prepared via sol-gel techniques, easily recovered and fluidised in treated effluent. It was used to degrade Procion Red MX-5B under UV illumination. It has been compared with commercial photocatalyst, Degussa P-25.</li> <li>- This photocatalyst was prepared using sol-gel techniques, easily fluidised and recovered using external magnetic field. The saturation magnetisation of this nanoparticle decreased as increasing the thickness of TiO<sub>2</sub> and the</li> </ul>	<p>(Chung, Park &amp; Kang 2004)</p> <p>(Xu et al. 2008)</p> <p>(Fu et al. 2005)</p> <p>(Fu et al. 2006b)</p>

	<ul style="list-style-type: none"> <li>- Barium ferrite</li> <li>- Zinc ferrite</li> <li>- M-type hexaferrite (M = Ba, Sr, Pb)</li> </ul>	<p>photocatalytic activity increased as increasing the thickness of TiO<sub>2</sub>. This nanoparticle has been used to degrade Procion Red MX-5B.</p> <ul style="list-style-type: none"> <li>- This photocatalyst was photoactive, with enhanced photocatalytic activity after the heat treatment for 500°C for 1 hour. This composite nanoparticle was used to degrade Procion red MX-5B under UV illumination.</li> <li>- This photocatalyst was prepared by sol-gel method. It has been found out that after being used four times during the photocatalytic reaction, TiO<sub>2</sub>/ZnFe<sub>2</sub>O<sub>4</sub> nanoparticles have good photocatalytic stability. It is used to degrade Rhodamine B under UV irradiation for 3 hours, and after 4 hours recycle, the catalyst did not exhibit any significant loss of activity.</li> <li>- This photocatalyst was easily recoverable using magnetic field, and the photocatalytic activity increased with increasing the thickness of TiO<sub>2</sub> coating layer. However, the saturation magnetisation of titania-coated BaFe<sub>12</sub>O<sub>19</sub> nanoparticles decreased with increasing thickness of TiO<sub>2</sub> coating. This composite nanoparticle was used to degrade Procion Red MX-5B under UV illumination.</li> </ul>	<p>(Lee et al. 2006)</p> <p>(Zhang, Zhang &amp; Feng 2008)</p> <p>(Fu et al. 2006a)</p>
Carbon	<ul style="list-style-type: none"> <li>- Iron-filled carbon nanocapsules</li> <li>- Magnetic activated carbon</li> </ul>	<ul style="list-style-type: none"> <li>- This photocatalyst produced by immobilization of TiO<sub>2</sub> nano-crystal onto Fe-Carbon nanocapsules. It avoids photodissolution of the iron core and enhances the performance in photocatalysis. Also, it displayed a good performance in NO gas removal and easy recycling.</li> <li>- This photocatalyst has been used to degrade phenol from treated water and has advantageous due to its recycling ability using external magnetic field. Even after 5 cycles, the degradation rate of phenol was still higher than 85%.</li> </ul>	<p>(Huang et al. 2006)</p> <p>(Ao et al. 2008)</p>
Polymers	<ul style="list-style-type: none"> <li>- Magnetic polymer microspheres</li> </ul>	<ul style="list-style-type: none"> <li>- This photocatalyst consisted of TiO<sub>2</sub> coated by magnetic poly (methyl methacrylate) or mPMMA microspheres. This study investigated the photocatalytic degradation of <i>p</i>-phenylenediamine (PPD) under various experimental conditions. This microsphere was employed as novel photocatalyst with the advantageous of high photocatalytic activity, magnetic separability and good durability.</li> </ul>	<p>(Chen et al. 2009c)</p>
Mixtures	<ul style="list-style-type: none"> <li>- Black sand (SiO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>,</li> </ul>	<ul style="list-style-type: none"> <li>- A photocatalyst consisted of TiO<sub>2</sub>, SiO<sub>2</sub>, and black sand was synthesized and magnetically recoverable. It removed various dyes such as</li> </ul>	<p>(Luo, Bowden &amp; Brimblecombe</p>

	$\gamma$ - Fe <sub>2</sub> O <sub>3</sub> , $\alpha$ -Fe	anionic dyes (Direct Red 80, Rose Bengal, Orange II, Eosin B) and cationic dyes (Rhodamine B, Ethyl Violet) through adsorption and photocatalytic oxidation. It has been found out that the removal by photocatalytic oxidation occurred with anionic dyes and strong adsorption occurred with cationic dyes.	2009)
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There are important magnetic properties to consider the development of good magnetic photocatalyst for water treatment application, where the magnetic cores should have a good dispersibility in aqueous phase, high coercivity, high saturation magnetisation, and an excellent chemical and mechanical stability (Beydoun 2000; Chen et al. 2009a). Among other magnetic cores which are shown at Table 2, iron oxide is the most investigated magnetic materials due to its excellent properties and its widespread applications in industry.

Magnetite ( $\text{Fe}_3\text{O}_4$ ) is a black mineral, ferrimagnetic material, non-toxic, widely spread in nature and one of several iron oxides with an inverse spinel structure (Beydoun 2000; Fleet 1981). In water purification, magnetite is mainly used as an adsorbent, where it is effective for the removal of arsenic in drinking water. Moreover, as a photocatalyst, according to (Chen, Rulkens & Bruning 1997), it effectively removes phenols and COD in industrial wastewaters.

For about a decade, the development of magnetic photocatalyst for environmental remediation has been numerously reported in literatures (Beydoun 2000; Beydoun & Amal 2002; Beydoun et al. 2001; Bruce et al. 2004; Buske 1994; Chambers, Droubay & Kaspar 2006; Chen, Deng & Zhang 2010; Chen et al. 2009a; Chen et al. 2009b; Chen et al. 2009c; Fukumura, Toyosaki & Yamada 2005; Gad-Allah et al. 2008; Gad-Allah et al. 2009; Hai 2009; He et al. 2008; Li et al. 2009; Nunes et al. 2006; Philipse, van Bruggen & Pathmamanoharan 1994; Tural, Ozkan & Volkan 2009; Watson, Beydoun & Amal 2002; Watson et al. 2005; Wen et al. 2009; Xu, Bao & Zhang 2005; Xu et al. 2007; Xu et al. 2008; Xuan et al. 2009; Zhang, Zhang & Feng 2008). However, this review paper is based on more into extensive studies on producing an ideal magnetic photocatalyst using magnetite and  $\text{TiO}_2$  as the raw materials (Beydoun et al. 2000; Chen et al. 2009a; Watson, Beydoun & Amal 2002; Watson et al. 2005). It was to believe that an ideal magnetic photocatalyst for water purification should have the following properties, namely, highly photoactive, chemically stable, inexpensive, reusable and environment friendly (Tryk, Fujishima & Honda 2000). The simple direct doping technique of photoactive  $\text{TiO}_2$  into magnetite core has been carried out by (Beydoun et al. 2000; Watson, Beydoun & Amal 2002; Watson et al. 2005) to produce a magnetic photocatalyst. However, it has been proven that direct deposition of  $\text{TiO}_2$  into the magnetite cores is ineffective due to photodissolution phenomenon of magnetite particles during UV irradiation. In order to prevent this photodissolution effect, it is necessary to cover and protect the magnetite particles using an inert material such as silicon dioxide ( $\text{SiO}_2$ ) as an intermediate layer before depositing highly photoactive  $\text{TiO}_2$  into the magnetic core. Furthermore, it has been proven that this insulation of  $\text{SiO}_2$  did not just inhibit the photodissolution effect and it also has no effect on the photoactivity during UV irradiation.

The synthesis or preparation of magnetised  $\text{TiO}_2$  will be explained further on the next section such as methods available for particle coating with advantages and disadvantages associated with each technique.

### **3. Preparation Techniques/ Synthesis of Magnetised $\text{TiO}_2$**

The concept of coating a material with another has gained a prominent approach. Nowadays, it becomes one of the most important developments of photocatalyst. The main purpose of particle coating is to modify the properties of the main material with another material in order to achieve the specific requirement or objective. For instance, in order to avoid the photodissolution effect due to highly photoactive  $\text{TiO}_2$ , silica coating is needed as intermediate layer to protect the magnetite core during UV irradiation (Beydoun 2000). There are number of methods available on the preparation of magnetised  $\text{TiO}_2$  and it has been categorised into two methods, namely wet-chemistry methods (sol-gel method and hydrothermal) and dry-chemistry methods (aerosol combustion and chemical vapour deposition (CVD)). In this review paper, the most common techniques for particle coating as well as the advantages and disadvantages associated with each method are shown in Table 3.

Table 3: Most common particle coating techniques to develop magnetised TiO<sub>2</sub>

<b>Particle Coating Method</b>	<b>Advantages</b>	<b>Disadvantages</b>	<b>Reference(s)</b>
Sol-gel method	<ul style="list-style-type: none"> <li>- Excellent chemical homogeneity</li> <li>- Easy to prepare a composite with organic materials</li> <li>- Lower temperature calcination</li> <li>- Easier and economical compared to CVD and sputtering deposition method</li> <li>- High purity of product</li> <li>- Uniform phase distribution in multicomponent systems due to high close control during early stage processing</li> </ul>	<ul style="list-style-type: none"> <li>- Number of steps required to achieve high purity of product e.g. difficult to remove solvent and organic byproducts from gel</li> <li>- Expensive alkoxide precursors are used as starting material</li> <li>- The volume shrinkage upon sol-gel transition is large</li> </ul>	(Beydoun 2000; Sakka 2004)
Hydrothermal synthesis	<ul style="list-style-type: none"> <li>- Inexpensive starting material and easy to handle</li> <li>- High monodispersity of the nanoparticles</li> <li>- High crystallinity of product at relatively low temperature</li> <li>- Controlled morphology, size and phase, composition, which lead to uniform particle distribution</li> </ul>	<ul style="list-style-type: none"> <li>- The necessity to use pressurized equipment such as expensive autoclave</li> </ul>	(Chen et al. 2009a; Cheng et al. 1995; Kontos et al. 2005)
Aerosol combustion technique	<ul style="list-style-type: none"> <li>- High purity of product due to high temperature flame environment</li> <li>- Flexible in producing a particle less than 10 nm or over several micron in size</li> <li>- No need extra process (e.g. washing) which can lead to less process waste and lower pollutant emissions</li> </ul>	<ul style="list-style-type: none"> <li>- Difficult to control the morphology of the coated particles due to extremely high temperatures required</li> </ul>	(Mayville, Partch & Matijevic 1987; Wooldridge 1998)
Chemical vapour deposition (CVD)	<ul style="list-style-type: none"> <li>- High dense and purity of product</li> <li>- Highly controlled the crystal structure, surface morphology and orientation of CVD products by controlling the parameters</li> <li>- Uniform films with good reproducibility and</li> </ul>	<ul style="list-style-type: none"> <li>- High production cost due to sophisticated reactor required for the process</li> <li>- Dangerous of chemical and safety hazards due to the toxicity,</li> </ul>	(Choy 2003; Powell, Kodas & Anderson 1996)

	adhesion at high deposition rates - Flexibility of using a wide range of chemical precursors such as halides, hydrides, organometallics which enable the deposition of a large spectrum of materials such as metal, carbides, nitrides, oxides, sulphides.	corrosive, flammable and/or explosive precursor gases - Difficult to deposit multicomponent materials with well controlled stoichiometry using multi-source precursors	
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However, in water purification system, despite of the highly purity of products which dry-chemistry method can offer, wet-chemistry methods are still favourable to be employed. It is because wet chemistry method offer simplicity in terms of equipment, slow reaction process which lead to excellent homogeneity of products and low temperature used which is cost-effective. For this review paper, the sol-gel method and hydrothermal method was chosen as a suitable particle coating method for developing a novel magnetised TiO<sub>2</sub>.

There are two steps involved in developing the novel magnetised TiO<sub>2</sub> (as previously mentioned in the last chapter), firstly, silica-coating onto the magnetite cores and finally, TiO<sub>2</sub> coating onto the silica-coated magnetite cores. The first up to final coating mechanism of magnetised TiO<sub>2</sub> can be shown and explained in Table 4.

Table 4: The Procedures to Develop Magnetised TiO<sub>2</sub> using Sol-Gel Method and Hydrothermal Method

Coating mechanism of Magnetised TiO <sub>2</sub>	Particle Coating Method	Reactant used	Reaction Parameters	Effect of reaction parameters	References
<b>1. Silica coating</b>	Sol-gel method (Stober method): - Hydrolysis - Condensation	Tetraethylorthosilicate (TEOS) as precursor in alcoholic media with water in the presence of certain bases.	- Reactant concentration	- Higher concentration leads to the increase in silica-shell thickness, surface area, wetting and dispersion of the magnetite in aqueous solvent but reduce magnetic attraction	(Donselaar & Philipse 1999; El-Toni, Yin & Sato 2006; Liu et al. 1998; Liu et al. 2008)
	Silicic acid method at pH = 10	Aqueous Sodium Silicate, hydrochloric acid (HCl), Tetramethylammonium	- Temperature		

		hydroxide (TMA)			
	Two step coating method: - Sol-gel method - Dense –Liquid Process	The reactant used is the same as above	- Time	- Higher temperature leads to the increase in silica-shell thickness and decrease in microporosity - Longer coating time leads to the increase in silica-shell thickness and decrease in microporosity	
<b>2. TiO<sub>2</sub> coating</b>	Sol-gel method: - Hydrolysis - Condensation	Titanium isopropoxide (TISOP) or titanium butoxide (TBOT) or titanium tetrachloride (TiCl <sub>4</sub> ) as precursor	- Reactant concentration  - Water concentration  - Relative number of core particles presents  - pH	- Higher reactant concentration leads to increase in the degree of saturation which resulted in heterogeneous system consisting of coated materials and freely TiO <sub>2</sub> particles rather than an increase in the coating's thickness - Increasing water concentration leads to the increase in the thickness of TiO <sub>2</sub> coating on the surface of the core particles and homogeneous system was achieved. However, if water concentration exceeds a critical value, it leads to the formation of free TiO <sub>2</sub> particles and heterogeneous system was occur. - Higher in number	(Aiken & Matijevic 1988; Beydoun 2000; Gherardi & Matijevic 1986; Hanprasopwattana et al. 1996; Haq & Matijevic 1997; Plaza et al. 1997)

			<ul style="list-style-type: none"> <li>- Aging time</li> <li>- Temperature</li> </ul>	<p>of core particles present leads to increase in number of available 'sites' of core to be deposited, therefore TiO<sub>2</sub> coating thickness can be controlled</p> <ul style="list-style-type: none"> <li>- Varying the pH affect the surface charge of core and shell particles and the reaction kinetics (rate of hydrolysis and condensation). If at certain pH, the surface charge of core and shell particles are the same, repulsion electrostatic force will exist which inhibit TiO<sub>2</sub> particles to be discharged from the magnetite cores.</li> <li>- Longer aging time leads to the increase in thickness of TiO<sub>2</sub> coating on magnetite cores</li> <li>- Varying temperature leads to the fully control of the rate of hydrolysis and the degree of saturation. It may also have an effect on the degree of interations such as Brownian motion effect.</li> </ul>	
	Hydrothermal	TiCl <sub>4</sub> as precursor	- Reactant	- Higher reactant	(Chen et al. 2009a;

	method		<p>concentration</p> <ul style="list-style-type: none"> <li>- pH</li> <li>- Aging time</li> <li>- Temperature</li> <li>- Heat treatment/ Calcination</li> </ul>	<p>concentration leads to the increase in acidity, therefore, increasing the proportion of anatase. Moreover, it also leads to the increase in degree of agglomeration which resulted in lower surface area.</p> <ul style="list-style-type: none"> <li>- Increasing pH leads to increase the proportion of anatase</li> <li>- Longer aging time leads to the increase of particle size and higher crystallinity</li> <li>- Higher temperature leads to the decrease in degree of agglomeration</li> <li>- Higher temperature in calcination leads to the increase of anatase crystallinity from amorphous TiO<sub>2</sub></li> </ul>	<p>Cheng et al. 1995; Li et al. 2010)</p>
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In literatures, it has been found out that silica coating on magnetite cores using sol-gel method or Stober method were not as effective as deposition of silica using silicic acid method (pH = 10), due to incomplete coating or porous particle (Bruce et al. 2004; Taylor et al. 2000). According to (Liu et al. 1998), two-step coating methods (coating by sol-gel method and followed by dense-liquid coating) were the best method to coat magnetite particles compared to just a single sol-gel method or silicic acid method. It has been reported that two-step coating method offers the highest protection against acid attack at the thinnest silica coatings with maximised magnetisation.

On the other hand, magnetised TiO<sub>2</sub> can be effectively synthesised using Sol-Gel method and hydrothermal method. Several works has been carried out on the preparation of TiO<sub>2</sub> for water and wastewater treatment application, and most of these published literature using expensive titanium alkoxides as a precursor (Beydoun 2000; Watson, Beydoun & Amal 2002; Watson et al. 2004; Watson et al. 2005; Zhang et al. 2008). Furthermore, this method has a number of disadvantages, namely, expensive precursor material, further heat treatment are required to obtain highly photoactive anatase crystalline phase, acidic and unstable anatase phase are obtained (Chen et al. 2009a; Cheng et al. 1995; Yanagisawa & Ovenstone 1999; Zhang et al. 2008).

In comparison to sol-gel method, hydrothermal method has shown great promising alternative route for TiO<sub>2</sub> coating preparation. It did not require expensive precursor and yield highly photoactive TiO<sub>2</sub> coating at lower temperature (Table 2). In terms of commercialisation potential, this method may be preferred over sol-gel method in developing novel magnetised TiO<sub>2</sub>. In the next chapter, the characterisation of magnetised TiO<sub>2</sub> produced from sol-gel route and hydrothermal method will be discussed thoroughly. Particle characterisation method and its utilities will be discussed and supported with tabulated data, graph and equation.



#### 4. Characterisation of Magnetised TiO<sub>2</sub>

Particle characterisation is the most important indication tools to determine the nature, shapes, size, phase and interaction of the particles. The main tools to examine or characterised the magnetised TiO<sub>2</sub> particles were shown and tabulated in Table 5.

Table 5: Most Common Characterisation Types and Methods for Magnetised TiO<sub>2</sub> with its Utilities

Particle Characterisation Type	Particle Characterisation Method	Utilities
Imaging	TEM, SEM, STEM	Analysed fine details of the particles, such as morphology
Graphic plot	XRD, XRF	Analysed the crystal phase and particle compositions
	BET Surface Area	Analysed the surface area of the composite magnetised TiO <sub>2</sub> by using nitrogen adsorption-desorption techniques
	Zeta Potential Analyser	Analysed the stabilisation of the particles in colloidal systems
	Photon Correlation Spectroscopy	Analysed the diameter of the particles using the dynamic light scattering techniques
	Vibrating sample Magnetometer	Analysed the degree of saturation magnetisation

The characterisation of magnetised TiO<sub>2</sub> will be examined based on morphology studies, crystallography studies, BET surface area, and particles mobilisation studies.

##### 4.1. Morphology studies

Transmission Electron Microscopy (TEM) is used to examine the fine details such as morphology, thickness of silica and TiO<sub>2</sub> coating on magnetite cores. There are two type of electron microscope used to characterise the particles such as JOEL 2000FX or Phillips CM200 at 160kV and 200 kV respectively. To achieve higher resolution of the image and better result, Phillips CM200 electron microscope is preferred because this microscope combines with Energy dispersive X-ray analysis (EDX), and therefore, STEM supported by X-ray mapping images, will provide information on the final resulting system (homogeneous or heterogeneous) and particles phase position.

For example, STEM images taken of magnetised TiO<sub>2</sub> particles with X-ray mapping (corresponding to iron (Fe), silica (Si) and titanium (Ti)) from conventional sol-gel and hydrothermal methods was shown at Figure 2 and 3 respectively. (Chen et al. 2009a; Watson, Beydoun & Amal 2002)

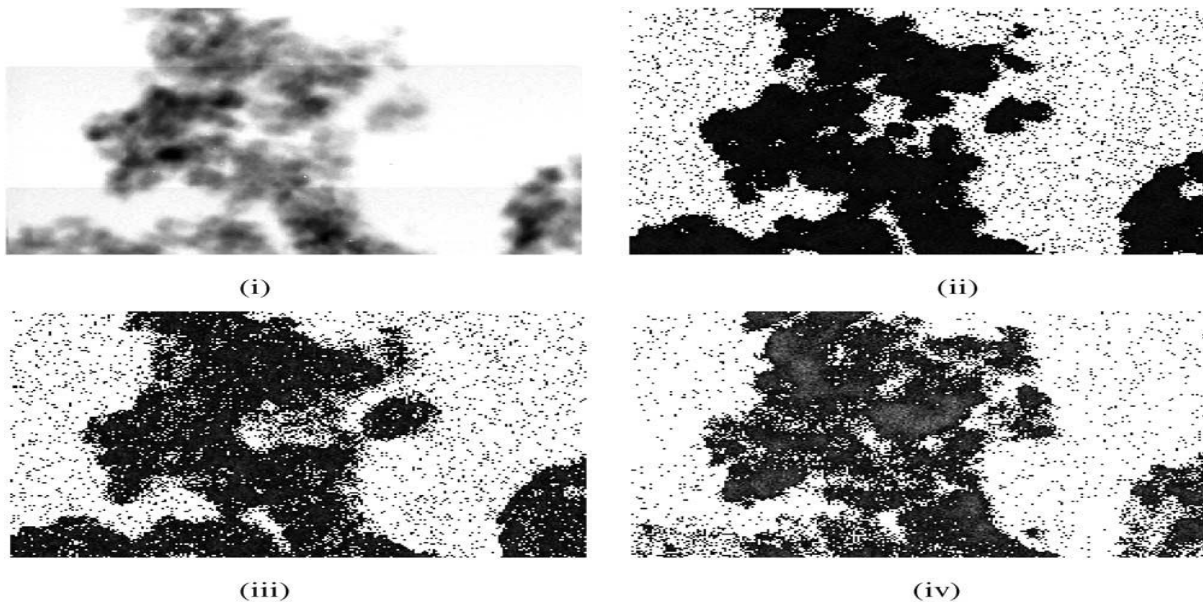


Figure 2: STEM Images of Magnetised TiO<sub>2</sub> Particles using Sol-Gel Method: (i) Magnetised TiO<sub>2</sub> particles, (ii) corresponding to Fe X-ray map, (iii) corresponding Si X-ray map, (iv) corresponding to Ti map (adopted from (Watson, Beydoun & Amal 2002))

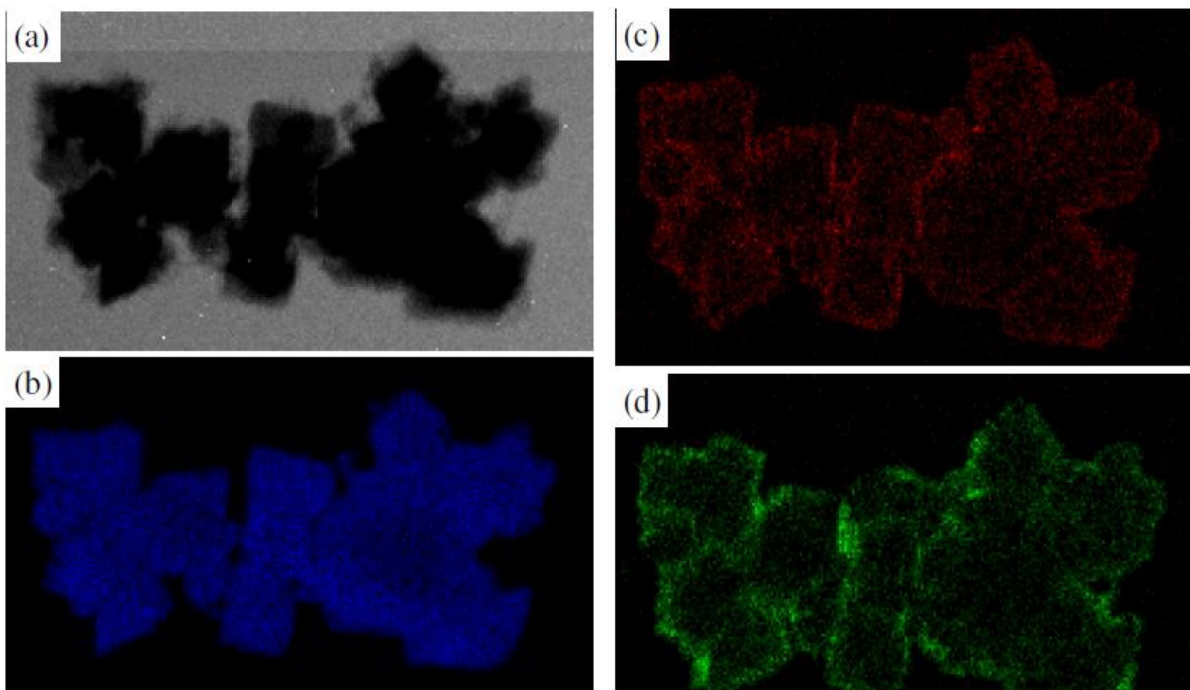


Figure 3: STEM Images of Magnetised TiO<sub>2</sub> Particles using Hydrothermal Method: (a) Magnetised TiO<sub>2</sub> particles, (b) corresponding to Fe X-ray map, (c) corresponding Si X-ray map, (d) corresponding to Ti map (adopted from (Chen et al. 2009a))

#### 4.2 Crystallography studies

The crystal structure phase and particle compositions of magnetised TiO<sub>2</sub> can be obtained by X-Ray diffraction (XRD) analysis. The instrument used for this study was Siemens D5000 Diffractometer. Figure 4 will show the result of XRD analysis of magnetised TiO<sub>2</sub> particles after calcination at 450°C for 1 hour.

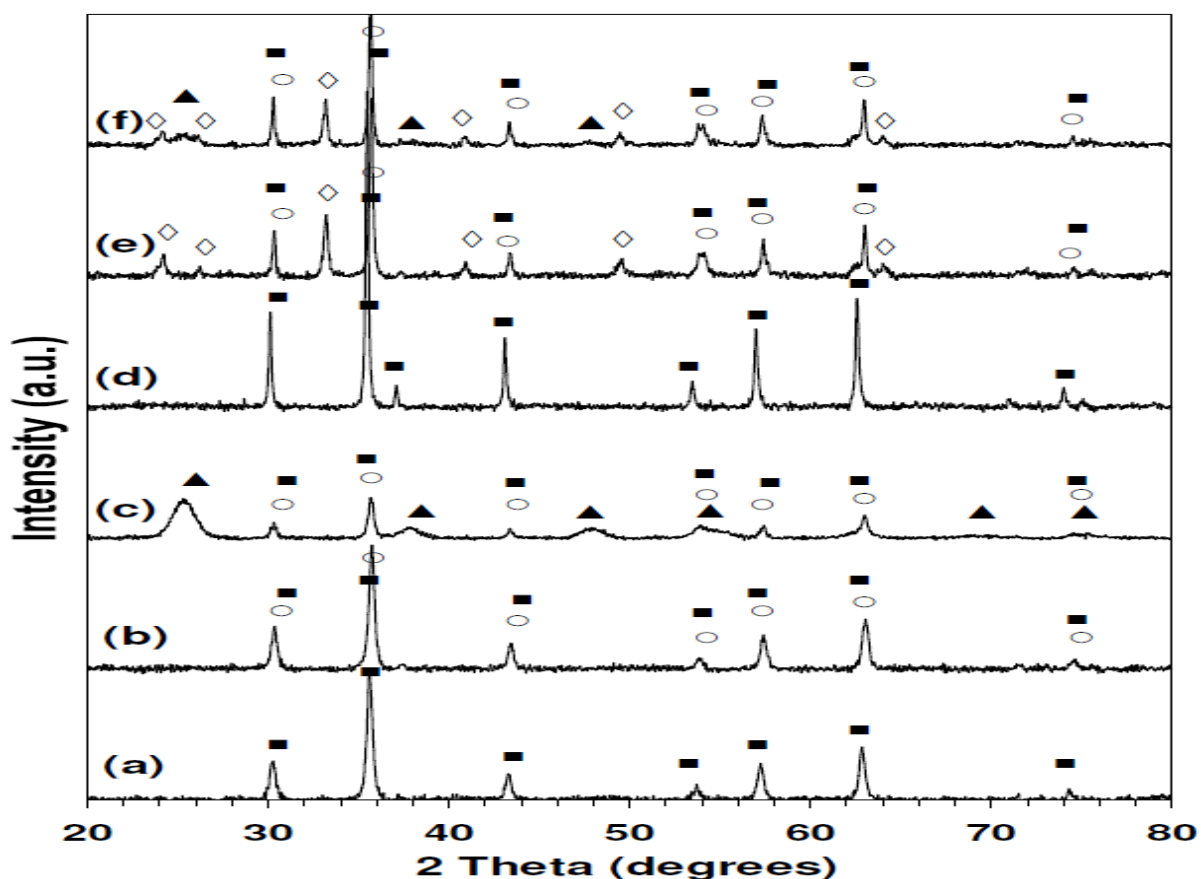


Figure 4: XRD Analysis of Magnetised TiO<sub>2</sub> Particles (micron and nano size) after Calcination at 450°C for 1 hour: (a) Nano-size Magnetite, (b) Nano-size Magnetite after Calcination, (c) Magnetised TiO<sub>2</sub> after Calcination, (d) Micron-size Magnetite, (e) Micron-size Magnetite after Calcination, (f) Magnetised TiO<sub>2</sub> after Calcination. ■ = Magnetite, ○ = Maghemite, ▲ = Anatase, ◇ = Hematite (adopted from (Chen et al. 2009a))

According to (figure 4(a), (b), (d), and (e)), both micron and nano-sized magnetite particles formed two extra partially-oxidised iron phases (maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) and hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>)) after calcination at 450°C for 1 hour. In principle, it is difficult to distinguish magnetite and maghemite in XRD analysis which was due to the same inverse spinel structure and lattice constant of these both iron oxide phases. It has been reported that the further oxidation of magnetite to maghemite and hematite can lead to decreasing in magnetic properties (Dang et al. 1998; Gao et al. 2003; Yanagisawa & Yamasaki 1991). However, (Chen et al. 2009a) has reported that there are no extra peaks occurred after calcination in XRD analysis (refer to Figure 4(c and f)) for both micron and nano-sized magnetised TiO<sub>2</sub> particles. It means that there was no formation of Fe/Ti mixed oxide system such as Fe<sub>2</sub>TiO<sub>5</sub> between TiO<sub>2</sub> and iron oxide interfaces (complete coating with silica), therefore, it can be assumed that complete insulation of silica onto the magnetite cores was achieved.

### 4.3 ET Surface area

Surface area and porosity are important characteristics in understanding the structure, formation and potential applications of the materials. Moreover, surface area of the particles

will mostly be depending on particle size. For instance, the smaller particles have a higher surface area compared to larger particles. Nitrogen adsorption-desorption isotherm technique was used to obtain particle surface area and calculated using the BET isotherm equation. In this review paper, this technique was also used to determine the composition (weight %) of magnetised TiO<sub>2</sub> based on the amount of nitrogen that can be adsorbed into the particles pores. Surface area of the photocatalyst particles will affect the photocatalytic activity, for instance, the higher the surface area provide more active sites, therefore it increase adsorption and degradation activity (Chen et al. 2009a).

The specific surface area can be calculated using BET isotherm equation and was expressed in the equation 1 below (Brunauer, Emmett & Teller 1938):

$$\frac{p}{v(p_o-p)} = \frac{1}{v_m c} + \frac{(c-1) p}{v_m c p_o} \quad \dots (1)$$

Where, p = equilibrium pressure of adsorbates, p<sub>o</sub> = saturation pressure of adsorbates, v = volume of gas adsorbed on one square centimetre of the particle surface, v<sub>m</sub> = volume of gas adsorbed for entire particles surface, c = BET constant

By plotting  $\frac{p}{v(p_o-p)}$  against  $\frac{p}{p_o}$  should give a linear equation, where the slope is  $\frac{(c-1)}{v_m c}$  and the intercept is  $\frac{1}{v_m c}$ . BET constant, c, can be expressed in equation 2 below:

$$c = e^{\left(\frac{E_1-E_L}{RT}\right)} \quad \dots (2)$$

Where, c = BET constant, E<sub>1</sub> = heat of first adsorption layer, E<sub>L</sub> = heat of liquefaction, R = gas constant (8.314 J/Kmol), T = Temperature in Kelvin (K = °C + 273 K)

#### 4.4 Particles Mobilisation Studies

Zeta potential measurement was used to analyse the stabilisation of particles in colloidal system as a function of pH. The instrument used is “ZetaPlus” from Brookhaven Instruments. The zeta potential of magnetised TiO<sub>2</sub> particles (micron-sized) measurement in the presence of electrolyte solution (5mM KNO<sub>3</sub>) can be shown in Figure 5.

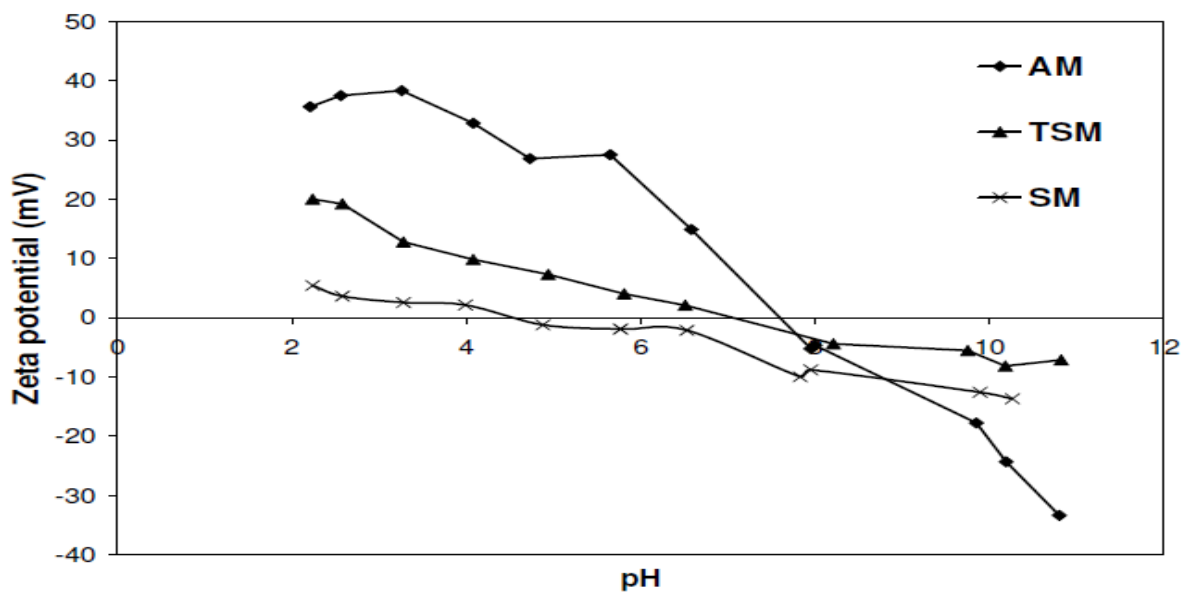


Figure 5: Zeta Potential of Magnetised TiO<sub>2</sub> (micron-size) as a function of pH. AM = Bare Magnetite, SM = Silica-Coated Magnetite, TSM = Magnetised TiO<sub>2</sub> (adopted from (Chen et al. 2009a))

Figure 5 has shown the isoelectric point (IEP) or zero point discharge of bare magnetite, silica-coated magnetite and TiO<sub>2</sub>/Silica-coated magnetite were at pH of 5, 7.6 and 7 respectively. The lower value of IEP of silica-coated magnetite obtained compared to IEP of bare magnetite implies that the surface characteristic of magnetite particles was fully coated by silica layer. In literatures, the IEP value of original silica particles and TiO<sub>2</sub> particles were reported to be in the range of 1.5 to 4.5 and in the range of 5.5 – 7.0 respectively (Chen et al. 2009a).

In the next chapter, examples of applications of magnetised TiO<sub>2</sub> photocatalyst in water purification are summarised. In sub topics, NOM removal and bacteria removal will be discussed thoroughly.

## 5. Application of Magnetised TiO<sub>2</sub>

TiO<sub>2</sub> photocatalyst has been used in many applications such as water treatment and air pollution control. And as it has been introduced earlier, photocatalytic treatment using TiO<sub>2</sub> catalyst for water purification offered more advantageous rather than conventional separation processes in terms of waste disposal and post-stage treatment. Highly photoactive of titanium dioxide shells can destroy organic contaminant in wastewater; however, despite of those great properties, the difficulty in separation phase limits TiO<sub>2</sub> catalyst to be implemented in real water purification application. Therefore, the development of novel magnetised TiO<sub>2</sub> was essential to overcome this separation difficulty.

In focus on water purification application, the concept of utilising magnetic properties in enhancing separation processes had been expressed in the Sirofloc process (Pavlova & Dobrevsky 2005) and MIEX technology (Semmens et al. 2000). The Sirofloc process was first developed in 1985 by CSIRO Australia and nowadays it had been only used for treatment of drinking water. This process removes dissolved coloured materials, heavy metals compounds and turbidity from raw water by flocculation with magnetite particles. The adsorption process occurred under acidic condition where the magnetite particles become positively charged thus drawing negatively charged materials into its surface. After adsorption process, magnetic field is introduced which causing the magnetite particles to form large and dense floc, thus rapid settling of the loaded magnetite in the bottom of clarifier. On the other hand, at high pH (11-12), the magnetite particles become negatively charged, thus repelled all attached pollutants and allowed this magnetite to be continually regenerated (Pavlova & Dobrevsky 2005).

MIEX (Magnetic Ion Exchange) process is another development based on magnetically assisted chemical separation process, and was first developed by Orica Watercare, SA Water Corporation and CSIRO in 1990 (Semmens et al. 2000). This process has been developed to remove natural organic matter (NOM) from effluent by employing ion exchange resin beads with a magnetised component within their structure operated in a continuous process. Moreover, it removed dissolved organic carbon (DOC), dissolved coloured materials, humic substances, heavy metals compounds, sulfides, bromides and alkalinity from raw water (Chen et al. 2007; Semmens et al. 2000; Slunjski, Bourke & O'Leary 2000). This ion exchange resin beads is easily regenerated by 2M sodium chloride (NaCl) solution (Semmens et al. 2000).

Indeed, many studies have demonstrated that  $\text{TiO}_2$  was the most promising and suitable photocatalyst due to its properties of all other semiconductors for widespread environmental remediation applications. In biological application,  $\text{TiO}_2$  used as a photocatalyst to destroy microbial organism such as *Escherichia Coli* (Matsunaga et al. 1985). In water purification application, photocatalytic oxidation treatment using  $\text{TiO}_2/\text{UV}$  system was used to remove a major contaminant in drinking water, namely natural organic matter (NOM).

## 5.1 NOM removal

NOM removal in water is essential for several reasons, because NOM can (Eikebrokk, Juhna & Østerhus 2006):

1. Affect the colour, taste and odour properties of water
2. Produce disinfection by-product (DBP) of various kinds such as trihalomethanes (THM) and haloacetic acid (HAA)
3. Affect the stability and removal of inorganic particles
4. Affect biostability and biological regrowth in distribution systems such as bacteria growth
5. Form a complex compound in water such as organometallic compound
6. Foul the membrane

In NOM removal, a suitable photocatalyst must fulfil two major criteria of NOM removal such as the redox potential of the  $\text{H}_2\text{O}/\bullet\text{OH}$  ( $E^\circ = 2.8 \text{ eV}$ ) couple falls within the band gap of the photocatalyst and the photocatalyst remains stable during treatment. Recent studies have revealed the significant photocatalytic degradation capability of  $\text{TiO}_2$  for NOM removal (Al-Rasheed 2005; Attia, Kadhim & Hussein 2008; Augugliaro et al. 2005; Bayarri et al. 2005; Bertelli & Selli 2004; Beydoun 2000; Beydoun et al. 1999; Beydoun et al. 2001; Chu, Choy & So 2007; Danion et al. 2006; Dillert, Bahnemann & Hidaka 2007; Essam et al. 2007; Faisal, Abu Tariq & Muneer 2007; Gad-Allah et al. 2009; Gaya & Abdullah 2008; Guillard et al. 1999; Gunlazuardi & Lindu 2005; Haque & Muneer 2003; Harada & Tanaka 2006; Herrmann 1999; Hoffmann et al. 1995; Horikoshi, Hidaka & Serpone 2001; Kim & Choi 2007; Ku, Lee & Wang 2006; Kwon et al. 2008; Mas et al. 2005; McCullagh et al. 2007; Mrowetz, Pirola & Selli 2003; Ollis 1985; Pelizzetti & Minero 1993; Qamar, Saquib & Muneer 2005; Rashed & El-Amin 2007; Reyes et al. 2006; Samarghandi et al. 2007; Selvam et al. 2007; Singh et al. 2007; Vorontsov, N. Savinov & Smirniotis 2000; Watson, Beydoun & Amal 2002; Watson et al. 2004; Watson et al. 2005; Zainal et al. 2005).

To provide a larger overview of the extent of the drinking water contamination, a consolidated summary of photocatalytic degradation of organic contaminants using  $\text{TiO}_2$  photocatalyst with various type of  $\text{TiO}_2$  catalysts used are tabulated in Table 6.

Class of Organic Contaminants	Organic substrate	Type of TiO <sub>2</sub> catalyst (Synthesis or Commercial brand)	Major finding(s)	References
Aldehydes	Formaldehyde	P-25 (Degussa)	The complete degradation of formaldehyde has been achieved using TiO <sub>2</sub> anatase powder. No reaction intermediates was produced.	(Peral & Ollis 1992)
Aromatics hydrocarbon	Cathecol	Carbon black-modified nano-size TiO <sub>2</sub> (Sol-gel method)	The photocatalytic activity was achieved approximately 1.5 times by using carbon black-modified nano TiO <sub>2</sub> photocatalyst compared to unmodified nano TiO <sub>2</sub> photocatalyst. The efficiency of photocatalytic degradation was improved by 9 times with the presence of ozone.	(Kwon et al. 2008)
	Phenol	Degauss Mark	Photodegradation of phenol was carried out at different pH (3.5, 7, and 11). The optimum efficiencies of phenol removal were about 76% at pH of 11 in UV/TiO <sub>2</sub> /H <sub>2</sub> O <sub>2</sub> system.	(Samarghandi et al. 2007)
	2-chlorophenol	P-25 (Degussa)	The degradation of 2-chlorophenol was faster using sonophotocatalysis treatment.	(Mrowetz, Pirola & Selli 2003)
			The decomposition rate of 2-chlorophenol increased with increasing external anodic bias voltage applied up to 0.0 V (versus SCE). However, the decomposition rate was not obviously improved when dissolved oxygen molecules (electron scavenger) present.	(Ku, Lee & Wang 2006)
	4-chlorophenol	- P-25 (Degussa), - Hombikat UV 100 (Sachtleben Chemie), - TiLCOM HC 120 (Tioxide), - TiONA PC 10 (Millennium Inorganic Chemicals)	Higher photocatalytic activity for 4-chlorophenol degradation was observed using TiONA PC 10 catalyst due to smaller surface area compared to other type of catalysts (P-25, Hombikat UV100, and TiLCOM HC 120).	(Guillard et al. 1999)
2,4-	P-25 (Degussa)	99% of 2, 4-dichlorophenol has been degraded effectively using	(Bayarri et	



	dichlorophenol		2 g/L of TiO <sub>2</sub> loading at 6 hours under UV irradiation. The optimum TiO <sub>2</sub> loading was found out to be 0.5 g/L. The best degradation rate was found to be at pH of 5.6.	al. 2005)
	Pentachlorophenol	Titanium (IV) bis (ethyl acetoacetato)-diisopropoxide as precursors (Sol-gel method + calcination)	The complete mineralisation of pentachlorophenol in aqueous solution was observed after 16 hours under UV irradiation.	(Gunlazuardi & Lindu 2005)
	4-Fluorophenols	P-25 (Degussa)	99% of 4-fluorophenols were effectively removed using P-25 (Degussa) under UV-A light irradiation at 90 minutes. Additions of oxidants (KIO <sub>4</sub> , KBrO <sub>3</sub> , H <sub>2</sub> O <sub>2</sub> , (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> and KClO <sub>3</sub> ) increase the photocatalytic activity significantly. KIO <sub>4</sub> was found out to be the most efficient oxidants among others.	(Selvam et al. 2007)
Carboxylic Acid	Monochloroacetic acid (MCAA)	Rhône-Poulenc DT-51 grade	Advanced oxidation based on O <sub>3</sub> in the present of TiO <sub>2</sub> increase the removal rate of MCAA. However, MCAA did not directly react with O <sub>3</sub> .	(Mas et al. 2005)
	Oxalic acid	TiO <sub>2</sub> (Soekawa Chemicals)	Synergistic effect of sonophotocatalysis was obtained in Ar atmosphere. H <sub>2</sub> O <sub>2</sub> is a key material for this effect, it accelerate sonophotocatalysis reaction, as well as the yield of CO <sub>2</sub> was twice larger compared to single photocatalysis and sonolysis reactions in an Ar atmosphere.	(Harada & Tanaka 2006)
	Phenoxy acetic acid	- P-25 (Degussa), - Hombikat UV 100 (Sachtleben Chemie) - PC 500 (Millenium Inorganic Chemicals), - TTP (Travancore Titanium Products, India)	The degradation rate of phenoxyacetic acid and 2,4,5-trichlorophenoxyacetic acid was influence by several factors such as type of photocatalyst, catalyst and substrate concentration, and pH. Degussa P-25 found to be the most efficient photocatalyst for the degradation compared to other type of catalyst (Hombikat UV100, PC500 and TTP).	(Singh et al. 2007)

Chloroanilines	2-chloroaniline	P-25 (Degussa)	Slower decomposition of 2-chloroaniline was observed at high pH in the UV/TiO <sub>2</sub> /H <sub>2</sub> O <sub>2</sub> system. pH is the key parameter to the rate of degradation of 2-chloroaniline. And increasing H <sub>2</sub> O <sub>2</sub> concentration decreasing overall reaction rate.	(Chu, Choy & So 2007)
Dyes	Acid orange 8 and Acid Red 1	P-25 (Degussa)	Sonophotocatalysis reaction increase in the degradation rate rather than photocatalysis followed by sonolysis.	(Mrowetz, Pirola & Selli 2003)
	Acridine orange and Ethidium bromide	- P-25 (Degussa), - Hombikat UV 100 (Sachtleben Chemie), - PC 500 (Millenium Inorganic Chemicals)	The photodegradation of selected dyes (Acridine orange and Ethidium bromide) was reported to be influence by catalyst type, pH, catalyst and substrate concentration and types of oxidant. It was found out that both selected days were effectively removed using Degussa P-25 compared to other type of catalysts (Hombikat UV 100 and PC 500). Highest efficiency of acridine orange and ethidium bromide were observed at pH 10 and 6 respectively. The maximum degradation rate of acridine orange and ethidium bromide were observed at 0.25 mM and in the range of 0.1 to 0.4 mM respectively.	(Faisal, Abu Tariq & Muneer 2007)
	Chrysoidine Y	<b>P-25 (Degussa)</b>	The degradation rates of Chrysoidine Y were found out to be influence by several operating parameters such as pH, catalyst and substrate concentrations, and the presence of oxidants (H <sub>2</sub> O <sub>2</sub> and KBrO <sub>3</sub> ). It was found out that Chrysoidine Y can be effectively removed using TiO <sub>2</sub> catalyst compared to ZnO catalyst.	(Qamar, Saquib & Muneer 2005)
	Methylene blue (basic blue 9), methyl orange, indigocarmine, and Chicago sky blue (direct blue 1)	Tetraisopropyl orthotitanate as precursor (acid catalysed sol-gel method)	The highest removal efficiency obtained were 98.5% from methyl orange, followed by indigo carmine (92.4%), methylene blue (90.3%), and Chicago sky blue (60.3%).	(Zainal et al. 2005)
	Remazole golden yellow	25-45 µm of Magnetised TiO <sub>2</sub>	The optimum operating conditions were found to be 2500 ppm TiO <sub>2</sub> catalyst loading and pH of 3. The complete decolourisation	(Gad-Allah et al. 2009)

	G, remazole brilliant blue R, and reactive orange 16	(42% of TiO <sub>2</sub> : 14 % of SiO <sub>2</sub> : 44% of Fe <sub>3</sub> O <sub>4</sub> ), in weight percentage.	and degradation of selected dyes achieved under optimum operating conditions within 45 minutes irradiation. The efficiency of TiO <sub>2</sub> composite particles was not significantly change even after several reuse.	
Ethers	Methyl <i>tert</i> -butyl ether (MBTE)	P-25 (Degussa)	Photocatalytic degradation of MTBE was carried out using sonolysis, photocatalysis and sonophotocatalysis in the presence of H <sub>2</sub> O <sub>2</sub> as the oxidants. The degradation of MTBE was influence by its intermediates (acetone, <i>tert</i> -butyl formate and <i>tert</i> -butyl alcohol) and hydroxyl radicals. And the highest degradation and mineralisation efficiency was achieved under H <sub>2</sub> O <sub>2</sub> photolysis at 254 nm.	(Bertelli & Selli 2004)
Fungicides	Fenamidone	Titanium isopropoxide as precursor (sol-gel method + calcination)	The photocatalytic degradation of fenamidone, leads to the formation of sulfate anions and eight type of carboxylic acid. This photocatalytic reaction was carried out in TiO <sub>2</sub> -coated optical fibre reactor.	(Danion et al. 2006)
Herbicides	Isoproturon	- P-25 (Degussa), - Hombikat UV 100 (Sachtleben Chemie) - PC 500 (Millenium Inorganic Chemicals), - TTP (Travancore Titanium Products, India)	The degradation rates of isoproturon were found out to be influence by several operating parameters such as pH, catalyst and substrate concentrations, and the presence of oxidants (H <sub>2</sub> O <sub>2</sub> and KBrO <sub>3</sub> ). Degussa P-25 found to be the most efficient photocatalyst for the degradation compared to other type of catalyst (Hombikat UV100, PC500 and TTP).	(Haque & Muneer 2003)
Ketones	Acetone	Hombikat UV 100 (Sachtleben Chemie)	Photocatalytic reaction has been carried out using vibrofluidised and multiple fixed-bed photocatalytic reactors. Both photocatalytic reactors were compared to each other and it was found out that photocatalytic activity achieved by vibrofluidised photocatalytic reactor was higher compared to multiple fixed-bed photocatalytic reactors. However, the use of ultrasound did not	(Vorontsov, N. Savinov & Smirniotis 2000)

			affect the degradation of acetone.	
Perfluoroaliphatics	Trifluoroacetic acid, Sulfonic acid of nonafluorobutane and heptadecafluorooctane	P-25 (Degussa)	Perfluorocarboxylic acids in the presence of acidic aqueous TiO <sub>2</sub> conditions can be degraded upon UV irradiation yielding CO <sub>2</sub> and fluoride anions. On the other hand, perfluorosulfonic acids were not degraded at all.	(Dillert, Bahnemann & Hidaka 2007)
Pharmaceuticals	Lincomycin	P-25 (Degussa)	The degradation of selected drug, lincomycin was carried out using hybrid system (solar photoreactor + membrane filtration). Membrane filtration was used to enhance separation of TiO <sub>2</sub> catalyst from aqueous medium.	(Augugliaro et al. 2005)
	Tetracycline		The degradation of antibiotics, tetracycline was carried out using three different light sources (UV lamp, Solarium and UV-A lamp) and it was found out that greater photooxidation occurred when UV lamp and Solarium were used. Total inactivation of the antibiotic was reached after 1 hour using UV lamp and Solarium irradiation.	(Reyes et al. 2006)
Polymers	Polyvinylpyrrolidone (PVP)	P-25 (Degussa)	Photocatalytic oxidation removes any remnant groups of lactam ring in the PVP structure. The opening of lactam ring from PVP was the initial step of primary amine and propanoic acid formations, which lead to the final formation of NH <sub>4</sub> <sup>+</sup> and NO <sub>3</sub> <sup>-</sup> ions together with CO <sub>2</sub> gas.	(Horikoshi, Hidaka & Serpone 2001)

Table 6: Summary of Photocatalytic Degradation of Organic Contaminants using TiO<sub>2</sub> Photocatalyst

Even though, most of organic contaminants can be effectively removed by photocatalytic oxidation treatment using  $\text{TiO}_2$  photocatalyst, the industrial-scale implementation of real water purification application is still relatively rare due to the high process energy requirements. The situation, however, is gradually changed. Recently, (Erdei, Arecrachakul & Vigneswaran 2008) has developed a new system which treated a model of wastewater using only about 10 kWh/L energy, far less than current commercial (Photox and Purifics) PCO technologies. Feasible PCO technologies require effective, chemically resistant, and inexpensive photocatalyst materials. Recently, a cost-effective and practical method to prepare magnetised  $\text{TiO}_2$  for NOM removal has been produced by using commercially viable raw materials such as Titanium tetrachloride ( $\text{TiCl}_4$ ) as a precursor, sodium silicate as silica coating materials and magnetite as magnetic cores (Chen et al. 2009a). This magnetised  $\text{TiO}_2$  has been reported to remove approximately 60% of natural organic matter (NOM) in river water. However, the effectiveness of NOM removal by magnetised  $\text{TiO}_2$  was still lower compared to single phase  $\text{TiO}_2$ . Therefore, the possibilities to develop a new magnetised  $\text{TiO}_2$  photocatalyst, which is inexpensive and has high NOM removal properties, are considered for the future research.

## 6. Conclusion

In conclusion, this review paper focused on 4 major parts, namely, background on the development of magnetised TiO<sub>2</sub>, preparation/synthesis, characterisation and applications of magnetised TiO<sub>2</sub> for water purification. Generally, for about four decades, many studies have been carried out on titanium dioxide (TiO<sub>2</sub>) as a photocatalyst for water purification, it shown that TiO<sub>2</sub> is a promising material to solve water purification problems. However, the TiO<sub>2</sub> photocatalyst may causes difficulties during the separation phase from water. Therefore, the development of novel magnetised TiO<sub>2</sub> photocatalyst was carried out to overcome this problem, yet increase the reusability of photocatalyst particles. There are many studies of magnetised TiO<sub>2</sub> photocatalysts and, this paper is the first to review the field with a focus on water purification.

In the development of novel magnetised TiO<sub>2</sub>, wet chemistry synthesis are preferred as a method of particle coating such as sol-gel method and hydrothermal method. The thinnest silica coatings with maximised magnetisation was achieved by two-step coating method (coating by sol-gel method and followed by dense-liquid coating) and it was found out to be the best method for silica coating on magnetite cores compared to single sol-gel synthesis or silicic acid synthesis. While, hydrothermal method was preferred over sol-gel method to coat highly photoactive TiO<sub>2</sub> shells onto silica-coated magnetite. It was due to expensive precursor was not required and this method yield highly photoactive TiO<sub>2</sub> coating at lower temperature. Moreover, in terms of commercialisation potential, this method may be preferred over sol-gel method in developing novel magnetised TiO<sub>2</sub>.

Particle characterisation of magnetised TiO<sub>2</sub> is the most important indication tools to determine the nature, shapes, size, phase and interaction of the particles. Particle characterisation method and its utilities are summarised in Table 5 and discussed thoroughly in sub-topics. Examples of applications of TiO<sub>2</sub> and magnetised TiO<sub>2</sub> photocatalyst in water purification are summarised in the last chapter of this review paper. The first commercial application which utilise magnetic properties in enhancing separation process had been expressed in Sirofloc Process and MIEX technology. In water purification application, photocatalytic oxidation treatment using TiO<sub>2</sub>/UV system was used to remove a major contaminant in drinking water, namely natural organic matter (NOM). A consolidated summary of photocatalytic degradation of organic contaminants using TiO<sub>2</sub> photocatalyst was shown at Table 6.

Recently, a cost-effective and practical method to prepare magnetised TiO<sub>2</sub> for NOM removal has been produced by using commercially viable raw materials, and this magnetised TiO<sub>2</sub> particle has been reported to remove approximately 60% of NOM in river water. However, the effectiveness of NOM removal by magnetised TiO<sub>2</sub> was still lower compared to single phase TiO<sub>2</sub>. Therefore, the possibilities to develop a new magnetised TiO<sub>2</sub> photocatalyst, which is inexpensive and has high NOM removal properties, are considered for the future research.

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