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Magnetised titanium dioxide (TiO_2) for water purification: preparation, characterisation and application

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ABSTRACT

The study of titanium dioxide (TiO_2) 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 jeopardise the use of this water treatment technology. Recently, the development and production of magnetised TiO_2 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_2. Many researchers have studied magnetised TiO_2 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_2 photocatalyst into the magnetic-coated particles is also emphasised. In addition, the characterisation of magnetised TiO_2 in terms of physicochemical properties and operating conditions produced by each technique are critically reviewed. Moreover, examples of applications of TiO_2 and magnetised TiO_2 photocatalyst in water purification are summarised. In general, the effectiveness of organic removal by magnetised TiO_2 is still lower compared to single phase TiO_2. The future prospect of this field is deliberated to develop a novel, economic and efficient magnetised TiO_2 photocatalyst, which has high organic removal properties.

Keywords: Photocatalyst; Purification; Characterisation; Magnetised TiO_2

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,

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many conventional technologies such as membrane filtration (microfiltration, ultrafiltration, nanofiltration, and reverse osmosis) and/or advanced oxidation processes (AOP) heterogeneous photocatalyst were widely used to remove undesirable natural organic matter (NOM) from natural and wastewater [1–3]. 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 compounds such as carbon dioxide (CO_2), water (H_2O), 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 [4].

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 PCO is described in Fig. 1.

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 ultraviolet (UV) radiation with a wavelength sufficient to displace electrons from the valence band of the catalyst; for titanium dioxide this is below 387.5 nm. When photocatalyst titanium dioxide (TiO_2) absorbs 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 PCO 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 it 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_2), is the most thoroughly investigated due to its excellent properties and also has attracted significant attention over the past four decades [5–11].

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 [12–15]. The comparisons between photocatalytic slurry-type reactors and immobilised-type reactors are described in Table 1.

In water and wastewater purification applications, photocatalytic reaction with TiO_2 can either be carried

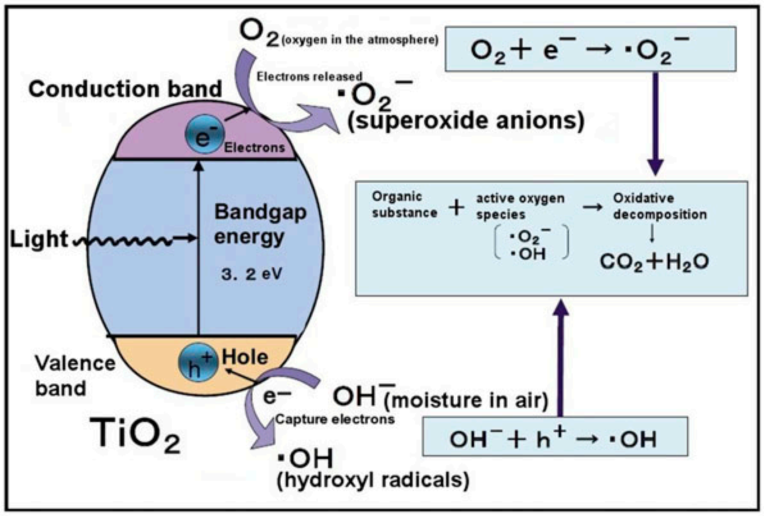

Fig. 1. The principle of PCO Process.

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

	Slurry-type reactors	Immobilised-type reactors
Advantages		
	• Fairly uniform catalyst distribution • High photocatalytic surface area to reactor volume ratio • Limited mass transfer • Minimum catalyst fouling effects due to the possible continuous removal and catalyst replacement • Well mixed particle suspension • Low pressure drop through the reactor	• Continuous operation • Improved removal of organic material from water phase while using a support with adsorption properties • No need for an additional catalyst separation operation
Disadvantages		
	• Requires post-process filtration • Important light scattering and adsorption in the particle suspended medium • Difficulty to recover the fine photocatalyst particles from treated effluent	• Low light utilisation efficiencies due to light scattering by immobilised photocatalyst • Restricted processing capacities due to possible mass transfer limitations • Possible catalyst deactivation and catalyst wash out

Note: Adopted from [15].

out in a slurry system or immobilised system. Despite its great properties it seems that TiO_2 may cause difficulties during the separation phase from water.

Although the slurry-type reactor was effective, it requires post-process a separation stage and additional chemicals, and it is difficult to recover the fine photocatalyst particles from the treated effluent, which limits the potential use of TiO_2 on a commercial scale [11,15]. There is 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_2 and its preparation techniques to coat magnetic materials is compared and discussed. The doping of photoactive TiO_2 photocatalyst into the coated magnetic materials is also emphasised. The characterisation of magnetised TiO_2 in terms of physicochemical properties and operating conditions produced by each technique is critically reviewed. Examples of applications of TiO_2 and magnetised TiO_2 photocatalyst in water purification are summarised.

2. Magnetised TiO_2

The semiconductor, TiO_2 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_2 [16]. According to Hoffmann [17], TiO_2 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_2 has been mainly used in the form of suspension or in the form of thin film [14,18–29].

There are two most common crystalline forms of TiO_2 which are used as photocatalyst, namely, rutile and anatase forms. Degussa P-25 is an example for commercially available TiO_2 photocatalyst, whose composition approximately consists of 25% rutile and 75% anatase form [30]. It has been used as a standard for photocatalytic degradation application in many studies [31]. Moreover, TiO_2 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 [32,33]. However, this form 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 [34], carbon [30,35], iron [36], and sulphur [37,38]. Photocatalysts doped with noble metals [39,40] show improved efficiency in the destruction of various compounds, compared to TiO_2 particles alone.

Although, 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 [7,11,13,22,27,41–61]. Various magnetic cores had been used to develop magnetic TiO_2 which is summarised in Table 2.

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 [59]. 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 (Fe_3O_4) is a black mineral, ferrimagnetic material, non-toxic, widely spread in nature and one of several iron oxides with an inverse spinel structure [59,76]. 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 et al. [77], 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 [7,11,13,22,27,41–51,53–61,78]. However, this review paper is based on more into extensive studies on producing an ideal magnetic photocatalyst using magnetite and TiO_2 as the raw materials [11,14,27,79]. 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 [16]. The simple direct doping technique of photoactive TiO_2 into magnetite core has been carried out by [11,14,27] to produce a magnetic photocatalyst. However, it has been proven that direct deposition of 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 (SiO_2) as an intermediate layer before depositing highly photoactive TiO_2 into the magnetic core. Furthermore, it has been proven that this insulation of 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 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 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 TiO_2, silica coating is needed as intermediate layer to protect the magnetite core during UV irradiation [59]. There are number of methods available on the preparation of magnetised 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.

However, in water purification system, despite the high purity of products which dry-chemistry method can offer, wet-chemistry methods are still favourable to be employed. It is because wet-chemistry methods offer simplicity in terms of equipment, slow reaction process which leads to excellent homogeneity of products and low temperature used which is cost-effective. For this review paper, the sol–gel method and hydrothermal method were chosen as suitable particle coating methods for developing a novel magnetised TiO_2.

There are two steps involved in developing the novel magnetised TiO_2, firstly, silica coating onto the magnetite cores and finally, TiO_2 coating onto the silica-coated magnetite cores. The first up to final coating mechanism of magnetised TiO_2 can be shown and explained in Table 4.

In literatures, it has been found that silica coating on magnetite cores using sol–gel method or Stober

Table 2
Various magnetic cores used to develop magnetised TiO_2

Magnetic photocatalyst cores type	Examples	Finding(s)	Reference(s)
Iron oxides	• Magnetite (Fe_3O_4)	• This photocatalyst was synthesised 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_2. The intermediate silica coating to prevent the photodissolution was also clearly described. This composite nanoparticles also used to degrade sucrose under UV illumination	[11,59]
	• Maghemite (γ-Fe_2O_3)	• 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℃ showed the highest activity for the degradation of aqueous solution of acridine dye	[62]
Metal ferrites	• Nickel ferrite	• This photocatalyst was prepared using continuous multi-step pyrolysis process. It has been used to photodegrade methylene blue (MB) for about 90 min per cycle. It has been found out that the photoactivity of the composite nanoparticle remained unchanged after magnetic separation and washing	[63]
		• A magnetically separable photocatalyst $TiO_2/SiO_2/NiFe_2O_4$ (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	[49]
	• Cobalt ferrite	• 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	[64]
		• Magnetic photocatalysts were synthesis by coating TiO_2–SiO_2 on cobalt ferrite ($CoFe_2O_4$) nanoparticles. The photocatalyst exhibits catalytic activity for the degradation of methylene blue dye in water under UV irradiation	[65]
	• Strontium ferrite	• 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_2 and the photocatalytic activity increased as increasing the thickness of TiO_2. This nanoparticle has been used to degrade Procion Red MX-5B	[64]
	• Barium ferrite	• This photocatalyst was photoactive, with enhanced photocatalytic activity after the heat treatment for 500°C for 1 h. This composite nanoparticle was used to degrade Procion red MX-5B under UV illumination	[66]
	• Zinc ferrite	• This photocatalyst was prepared by sol–gel method. It has been found out that after being used four times during the photocatalytic reaction, $TiO_2/ZnFe_2O_4$ nanoparticles have good photocatalytic stability. It is used to degrade	[48]

(*Continued*)

Table 2
(*Continued*)

Magnetic photocatalyst cores type	Examples	Finding(s)	Reference(s)
		Rhodamine B under UV irradiation for 3 h, and after 4 h recycle, the catalyst did not exhibit any significant loss of activity	
	• M-type hexaferrite (M = Ba, Sr, Pb)	• This photocatalyst was easily recoverable using magnetic field, and the photocatalytic activity increased with increasing the thickness of TiO_2 coating layer. However, the saturation magnetisation of titania-coated $BaFe_{12}O_{19}$ nanoparticles decreased with increasing thickness of TiO_2 coating. This composite nanoparticle was used to degrade Procion Red MX-5B under UV illumination	[67]
Carbon	• Iron-filled carbon nanocapsules	• This photocatalyst produced by immobilisation of TiO_2 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	[68]
	• Magnetic activated carbon	• 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%	[69]
	• TiO_2 loaded magnetic activated carbon	• First magnetite and then titania were deposited onto the activated carbon support by impregnation and sol–gel methods. It showed high activity in photocatalytic ozonation with complete removal of metoprolol tartrate in less than 2 h reaction time and 85% mineralisation after 5 h. This catalyst was also easily separable due to its developed magnetic properties	[70]
Polymers	• Magnetic polymer microspheres	• This photocatalyst consisted of TiO_2 coated by magnetic poly (methyl methacrylate) or mPMMA microspheres. This study investigated the photocatalytic degradation of *p*-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	[44]
Mixtures	• Black sand (SiO_2, Fe_3O_4, γ- Fe_2O_3, α-Fe)	• A photocatalyst consisted of TiO_2, SiO_2, and black sand was synthesised and magnetically recoverable. It removed various dyes such as anionic dyes (Direct Red 80, Rose Bengal, Orange II, and Eosin B) and cationic dyes (Rhodamine B, Ethyl Violet) through adsorption	[21]
	• Cobalt(II) phthalocyanine-sensitised hollow Fe_3O_4@SiO_2@TiO_2	• The catalyst was obtained by combination of solvothermal processing and dipping processing. The catalyst showed excellent photocatalytic efficiency for the degradation of methylene blue under UV–vis and visible light irradiation	[71]
	• Core-shell structured TiO_2/ SiO_2@Fe_3O_4	• The photocatalysts were prepared using Fe3O4 as magnetic core, tetraethoxysilane as silica source and tetrabutyl titanate as titanium sources. The photocatalyst exhibited an excellent performance for the complete degradation of methyl orange and methylene blue dye in 60 min under UV irradiation	[72]

(*Continued*)

Table 2
(*Continued*)

Magnetic photocatalyst cores type	Examples	Finding(s)	Reference(s)
	• Nano composite based on Fe@C	• Metallic/carbidic Fe@C nanoparticles submicronic aggregates embedded in/surrounded by defective and porous SiO_2 or TiO_2 matrices/shells were synthesised by laser pyrolysis followed by sol–gel method	[73]
	• $TiO_2/GO/SrFe_{12}O_{19}$	• This photo catalyst was synthesised via the solid reaction of silica (SiO_2)-coated $SrFe_{12}O_{19}$ with TiO_2 and GO, which were produced by a hydrothermal reaction and Hummer's method, respectively. The photoactivity was evaluated under direct sunlight for the degradation of 2,4-dichlorophenol over a period of 5 h with excellent photoactivity	[74]
	• MagCNTs@TiO_2 composites	• The composites were synthesised through a facile but effective solvothermal reaction for selective enrichment of phosphopeptides. The high magnetic susceptibility allowed convenient separation of the target peptides by magnetic separation	[75]

method was not as effective as deposition of silica using silicic acid method (pH 10), due to incomplete coating or porous particle [57,97]. According to Liu et al. [90], two-step coating methods (coating by sol–gel method and followed by dense liquid coating) were the best methods 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_2 can be effectively synthesised using sol–gel method and hydrothermal method. Several works has been carried out on the preparation of TiO_2 for water and wastewater treatment application, and most of these published literature using expensive titanium alkoxides as a precursor [11,27,59,98,99]. 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 phases are obtained [79,81,99,100].

In comparison to sol–gel method, hydrothermal method has shown great promising alternative route for TiO_2 coating preparation. It did not require expensive precursor and yields highly photoactive TiO_2 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_2. In the next chapter, the characterisation of magnetised TiO_2 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_2

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_2 particles were shown and tabulated in Table 5.

The characterisation of magnetised TiO_2 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_2 coating on magnetite cores. There are two types of electron microscope used to characterise the particles such as JOEL 2000FX or Phillips CM200 at 160 kV and 200 kV, respectively. To achieve higher resolution of the image and better result, Phillips CM200 electron microscope is preferred

Table 3
Most common particle coating techniques to develop magnetised TiO_2

Particle coating method	Advantages	Disadvantages	Reference(s)
Sol–gel method	• Excellent chemical homogeneity • Easy to prepare a composite with organic materials • Lower temperature calcination • Easier and economical compared to CVD and sputtering deposition method • High purity of product • Uniform phase distribution in multicomponent systems due to high close control during early stage processing	• Number of steps required to achieve high purity of product e.g. difficult to remove solvent and organic by-products from gel • Expensive alkoxide precursors are used as starting material • The volume shrinkage upon sol–gel transition is large	[59,80]
Hydrothermal synthesis	• Inexpensive starting material and easy to handle • High monodispersity of the nanoparticles • High crystallinity of product at relatively low temperature • Controlled morphology, size and phase, composition, which lead to uniform particle distribution	• The necessity to use pressurised equipment such as expensive autoclave	[79,81,82]
Aerosol combustion technique	• High purity of product due to high temperature flame environment • Flexible in producing a particle less than 10 nm or over several micron in size • No need extra process (e.g. washing) which can lead to less process waste and lower pollutant emissions	• Difficult to control the morphology of the coated particles due to extremely high temperatures required	[83,84]
Chemical vapour deposition (CVD)	• High dense and purity of product • Highly controlled the crystal structure, surface morphology and orientation of CVD products by controlling the parameters • Uniform films with good reproducibility and 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	• High production cost due to sophisticated reactor required for the process • Dangerous of chemical and safety hazards due to the toxicity, corrosive, flammable and/or explosive precursor gases • Difficult to deposit multicomponent materials with well controlled stoichiometry using multi-source precursors	[85,86]

Table 4
The procedures to develop magnetised TiO_2 using sol–gel method and hydrothermal method

Coating mechanism of magnetised TiO_2	Particle coating method	Reactant used	Reaction parameters	Effect of reaction parameters	References
1. Silica coating	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	[87–90]
	Silicic acid method at pH = 10	Aqueous sodium silicate, hydrochloric acid (HCl), Tetramethylammonium hydroxide (TMA)	• Temperature	• Higher temperature leads to the increase in silica-shell thickness and decrease in microporosity	
	Two step coating method: • Sol–gel method • Dense liquid process	The reactant used is the same as above	• Time	• Longer coating time leads to the increase in silica-shell thickness and decrease in microporosity	
2. TiO_2 coating	Sol–gel method: • Hydrolysis • Condensation	Titanium isopropoxide (TISOP) or titanium butoxide (TBOT) or titanium tetrachloride ($TiCl_4$) as precursor	• Reactant concentration	• Higher reactant concentration leads to increase in the degree of saturation which resulted in heterogeneous system consisting of coated materials and freely TiO_2 particles rather than an increase in the coating's thickness	[59,91–95]
			• Water concentration	• Increasing water concentration leads to the increase in the thickness of TiO_2 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_2 particles and heterogeneous system was occur	
			• Relative number of core particles presents	• Higher in number of core particles present leads to increase in number of available "sites" of core to be deposited, therefore TiO_2 coating thickness can be controlled	
			• pH	• Varying the pH affect the surface charge of core and shell particles and the reaction kinetics (rate of	

(Continued)

Table 4
(*Continued*)

Coating mechanism of magnetised TiO_2	Particle coating method	Reactant used	Reaction parameters	Effect of reaction parameters	References
				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_2 particles to be discharged from the magnetite cores	
			• Aging time	• Longer aging time leads to the increase in thickness of TiO_2 coating on magnetite cores	
			• Temperature	• Varying temperature leads to the full control of the rate of hydrolysis and the degree of saturation. It may also have an effect on the degree of interactions such as Brownian motion effect	
	Hydrothermal method	$TiCl_4$ as precursor	• Reactant concentration	• Higher reactant 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	[79,81,96]
			• pH	• Increasing pH leads to increase the proportion of anatase	
			• Aging time	• Longer aging time leads to the increase of particle size and higher crystallinity	
			• Temperature	• Higher temperature leads to the decrease in degree of agglomeration	
			• Heat treatment/ Calcination	• Higher temperature in calcination leads to the increase of anatase crystallinity from amorphous TiO_2	

Table 5
Most Common Characterisation Types and Methods for Magnetised TiO_2 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_2 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

because this microscope combines with energy dispersive X-ray analysis, 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_2 particles with X-ray mapping (corresponding to iron (Fe), silica (Si) and titanium (Ti)) from conventional sol–gel and hydrothermal methods are shown in Figs. 2 and 3, respectively [27,79].

4.2. Crystallography studies

The crystal structure phase and particle compositions of magnetised TiO_2 can be obtained by X-ray diffraction (XRD) analysis. The instrument used for this study was Siemens D5000 Diffractometer. Fig. 4 will show the result of XRD analysis of magnetised TiO_2 particles after calcination at 450˚C for 1 h.

According to Fig. 4(a–e), both micron and nanosized magnetite particles formed two extra partially oxidised iron phases (maghemite (γ-Fe_2O_3) and hematite (α-Fe_2O_3)) after calcination at 450˚C for 1 h. 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 [62,101,102]. However, Liu [79]

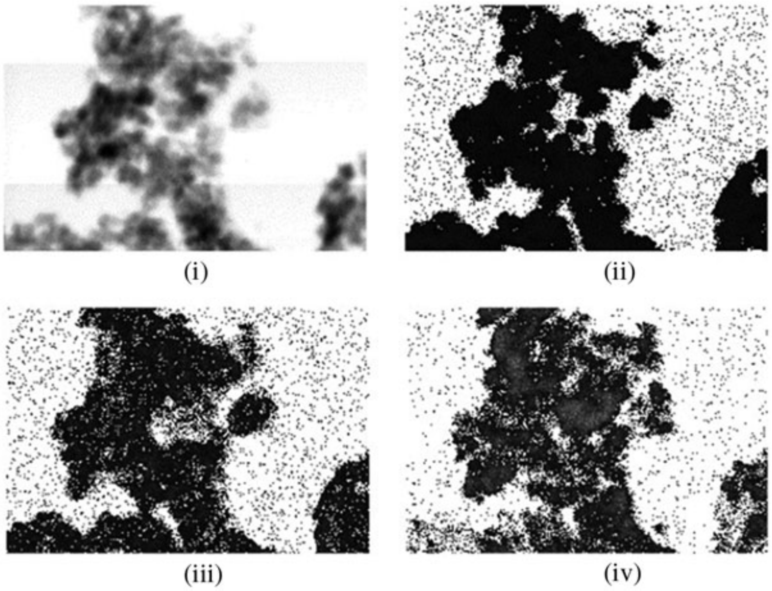

Fig. 2. STEM Images of magnetised TiO_2 particles using sol–gel method: (i) magnetised TiO_2 particles, (ii) corresponding to Fe X-ray map, (iii) corresponding Si X-ray map, and (iv) corresponding to Ti map (adopted from [27]).

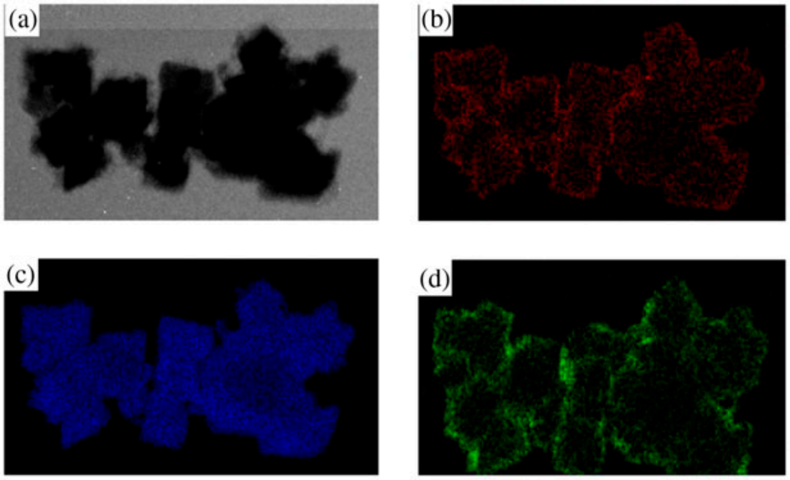

Fig. 3. STEM images of magnetised TiO_2 particles using hydrothermal method: (a) magnetised TiO_2 particles, (b) corresponding to Fe X-ray map, (c) corresponding Si X-ray map, and (d) corresponding to Ti map (adopted from [79]).

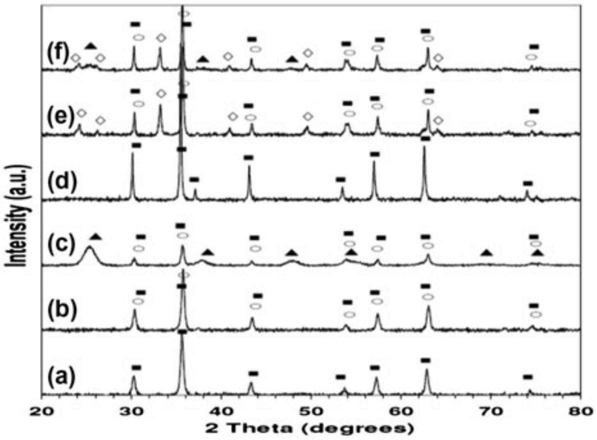

Fig. 4. XRD analysis of magnetised TiO_2 particles (micron and nanosize) after calcination at 450°C for 1 h: (a) nanosize magnetite, (b) nanosize magnetite after calcination, (c) magnetised TiO_2 after calcination, (d) micron-size magnetite, (e) micron-size magnetite after calcination, (f) magnetised TiO_2 after calcination. ■ = magnetite, ○ = maghemite, ▲ = anatase, ◇ = hematite (adopted from [79]).

has reported that there are no extra peaks occurred after calcination in XRD analysis (refer to Fig. 4((c) and (f))) for both micron and nanosized magnetised TiO_2 particles. It means that there was no formation of Fe–Ti mixed oxide system such as Fe_2TiO_5 between TiO_2 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. Bet 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_2 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 [79].

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_2 particles (micron-sized) measurement in the presence of electrolyte solution (5 mM KNO_3) can be shown in Fig. 5.

Fig. 5 shows the isoelectric point (IEP) or zero point discharge of bare magnetite, silica-coated magnetite, and TiO_2/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.

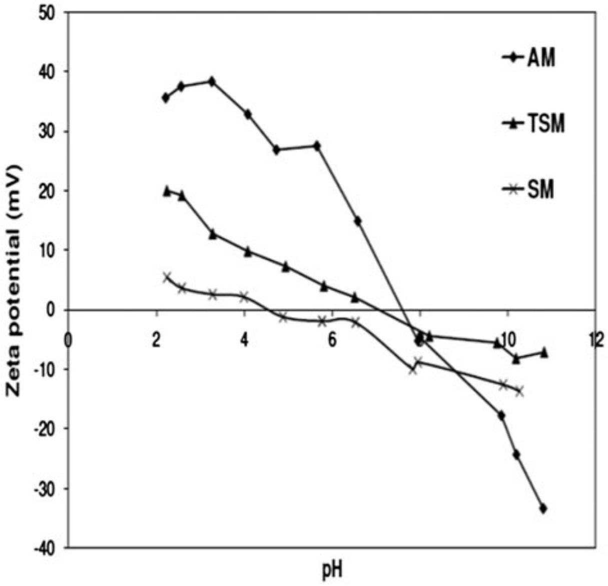

Fig. 5. Zeta potential of magnetised TiO_2 (micron-size) as a function of pH. AM = Bare magnetite, SM = silica-coated magnetite, TSM = magnetised TiO_2 (adopted from [103]).

In literatures, the IEP value of original silica particles and TiO_2 particles were reported to be in the range of 1.5–4.5 and in the range of 5.5–7.0 respectively [103].

In the next chapter, examples of applications of magnetised TiO_2 photocatalyst in water purification are summarised. In sub topics, NOM removal and bacteria removal will be discussed thoroughly.

5. Application of magnetised TiO_2

TiO_2 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_2 catalyst for water purification offered more advantages rather than conventional separation processes in terms of waste disposal and post-stage treatment. Highly photoactive titanium dioxide shells can destroy organic contaminant in wastewater; however, despite those great properties, the difficulty in separation phase limits TiO_2 catalyst to be implemented in real water purification application. Therefore, the development of novel magnetised TiO_2 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 [104] and MIEX technology [105]. 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 causes 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 [104].

Magnetic Ion Exchange (MIEX) 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 [105]. This process has been developed to remove 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, dissolved coloured materials, humic substances, heavy metals compounds, sulphides, bromides, and alkalinity from raw water [105,106]. These ion-exchange resin beads are easily regenerated by 2 M sodium chloride (NaCl) solution [105].

Indeed, many studies have demonstrated that 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, TiO_2 used as a photocatalyst to destroy microbial organism such as *Escherichia Coli* [105,107]. In water purification application, PCO treatment using TiO_2/UV system was used to remove a major contaminant in drinking water, namely (NOM).

5.1. Nom removal

NOM removal in water is essential for several reasons, because NOM can [108]:

(1) Affect the colour, taste and odour properties of water.
(2) Produce disinfection by-product of various kinds such as trihalomethanes and haloacetic acid.
(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 organ ometallic compound.
(6) Foul the membrane.

Table 6
Summary of photocatalytic degradation of organic contaminants using TiO_2 photocatalyst

Class of organic contaminants	Organic substrate	Type of TiO_2 catalyst (Synthesis or Commercial brand)	Major finding(s)	References
Aldehydes	Formaldehyde	P-25 (Degussa)	The complete degradation of formaldehyde has been achieved using TiO_2 anatase powder. No reaction intermediates was produced	[137]
Aromatics hydrocarbon	Cathecol	Carbon black-modified nano-size TiO_2 (Sol–gel method)	The photocatalytic activity was achieved approximately 1.5 times by using carbon black-modified nano TiO_2 photocatalyst compared to unmodified nano TiO_2 photocatalyst. The efficiency of photocatalytic degradation was improved by 9 times with the presence of ozone	[24]
	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 $UV/TiO_2/H_2O_2$ system	[25]
	2-Chlorophenol	P-25 (Degussa)	The degradation of 2-chlorophenol was faster using sonophotocatalysis treatment	[112]
			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	[117]
	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)	[118]
	2,4-Dichlorophenol	P-25 (Degussa)	99% of 2, 4-dichlorophenol has been degraded effectively using 2 g/L of TiO_2 loading at 6 h under UV irradiation. The optimum TiO_2 loading was found out to be 0.5 g/L. The best degradation rate was found to be at pH of 5.6	[131]

(*Continued*)

Table 6
(*Continued*)

Class of organic contaminants	Organic substrate	Type of TiO_2 catalyst (Synthesis or Commercial brand)	Major finding(s)	References
	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 h under UV irradiation	[130]
	4-Fluorophenols	P-25 (Degussa)	99% of 4-fluorophenols were effectively removed using P-25 (Degussa) under UV-A light irradiation at 90 min. Additions of oxidants (KIO_4, $KBrO_3$, H_2O_2, $(NH_4)_2S_2O_8$ and $KClO_3$) increase the photocatalytic activity significantly. KIO_4 was found out to be the most efficient oxidants among others	[132]
Carboxylic acid	Monochloro-acetic acid (MCAA)	Rhône-poulenc DT-51 grade	Advanced oxidation based on O_3 in the present of TiO_2 increase the removal rate of MCAA. However, MCAA did not directly react with O_3	[128]
	Oxalic acid	TiO_2 (Soekawa chemicals)	Synergistic effect of sonophotocatalysis was obtained in Ar atmosphere. H_2O_2 is a key material for this effect, it accelerate sonophotocatalysis reaction, as well as the yield of CO_2 was twice larger compared to single photocatalysis and sonolysis reactions in an Ar atmosphere	[113]
	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)	[129]
Chloroanilines	2-Chloroaniline	P-25 (Degussa)	Slower decomposition of 2-chloroaniline was observed at high pH in the $UV/TiO_2/H_2O_2$ system. pH is the key parameter to the rate of degradation of 2-chloroaniline. And increasing H_2O_2 concentration decreasing overall reaction rate	[114]

(*Continued*)

Table 6
(*Continued*)

Class of organic contaminants	Organic substrate	Type of TiO_2 catalyst (Synthesis or Commercial brand)	Major finding(s)	References
Dyes	Acid orange 8 and Acid Red 1	P-25 (Degussa)	Sonophotocatalysis reaction increase in the degradation rate rather than photocatalysis followed by sonolysis	[112]
	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	[121]
	Chrysoidine Y	P-25 (Degussa)	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_2O_2 and $KBrO_3$). It was found out that Chrysoidine Y can be effectively removed using TiO_2 catalyst compared to ZnO catalyst	[120]
	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%)	[133]
	Methyl orange	$C/TiO_2/Ni$ composite	The photocatalyst exhibited greater removal activity for Methyl Orange (MO) dye from water as compared with the commercially available well reported TiO_2 nanoparticles (P25)	[138]
		25–45 μm of Magnetised TiO_2 (42% of TiO_2 : 14 %	The optimum operating conditions were found to be	[22]

(*Continued*)

Table 6
(*Continued*)

Class of organic contaminants	Organic substrate	Type of TiO_2 catalyst (Synthesis or Commercial brand)	Major finding(s)	References
	Remazole golden yellow G, remazole brilliant blue R, and reactive orange 16	of SiO_2 : 44% of Fe_3O_4), in weight percentage.	2,500 ppm TiO_2 catalyst loading and pH of 3. The complete decolourisation and degradation of selected dyes achieved under optimum operating conditions within 45 min irradiation. The efficiency of TiO_2 composite particles was not significantly change even after several reuse	
Ethers	Methyl *tert*-butyl ether (MBTE)	P-25 (Degussa)	Photocatalytic degradation of MTBE was carried out using sonolysis, photocatalysis and sonophotocatalysis in the presence of H_2O_2 as the oxidants. The degradation of MTBE was influence by its intermediates (acetone, *tert*-butyl formate and *tert*-butyl alcohol) and hydroxyl radicals. And the highest degradation and mineralisation efficiency was achieved under H_2O_2 photolysis at 254 nm	[134]
Fungicides	Fenamidone	Titanium isopropoxide as precursor (sol–gel method + calcination)	The photocatalytic degradation of fenamidone, leads to the formation of sulphate anions and eight type of carboxylic acid. This photocatalytic reaction was carried out in TiO_2-coated optical fibre reactor	[122]
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_2O_2 and $KBrO_3$). Degussa P-25 found to be the most efficient photocatalyst for the degradation compared to other type of catalyst (Hombikat UV100, PC500 and TTP)	[123]
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	[135]

(*Continued*)

Table 6
(*Continued*)

Class of organic contaminants	Organic substrate	Type of TiO_2 catalyst (Synthesis or Commercial brand)	Major finding(s)	References
			reactor was higher compared to multiple fixed-bed photocatalytic reactors. However, the use of ultrasound did not affect the degradation of acetone	
Perfluoroaliphatics	Trifluoroacetic acid, sulphonic acid of nonafluorobutane and heptadecafluorooctane	P-25 (Degussa)	Perfluorocarboxylic acids in the presence of acidic aqueous TiO_2 conditions can be degraded upon UV irradiation yielding CO_2 and fluoride anions. On the other hand, perfluorosulfonic acids were not degraded at all	[115]
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_2 catalyst from aqueous medium	[136]
	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 h using UV lamp and Solarium irradiation	[124]
	Bioshop A and dibutyl phthalate	Tetrabutyl titanate	The degradation and mineralisation of the organics, bisphenol A and dibutyl phthalate, under UV illumination, and the magnetism associated with the 9 nm crystalline Fe_3O_4 core allows for the magnetic separation from the dispersion once photocatalytic degradation is complete	[139]
Polymers	Polyvinylpyrollidone (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_4^+ and NO_3^- ions together with CO_2 gas	[125]

In NOM removal, a suitable photocatalyst must fulfil two major criteria of NOM removal such as the redox potential of the $H_2O/\bullet OH$ ($E^{\circ} = 2.8\,\text{eV}$) 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 TiO_2 for NOM removal [1,6,11,13,17,22,24,25,27,32,38,59,98,109–136].

To provide a larger overview of the extent of the drinking water contamination, a consolidated summary of photocatalytic degradation of organic contaminants using TiO_2 photocatalyst with various type of TiO_2 catalysts used are tabulated in Table 6.

Even though, most of organic contaminants can be effectively removed by PCO treatment using 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, [140] has developed a new system in which a model of wastewater is treated 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 TiO_2 for NOM removal has been produced by using commercially viable raw materials such as Titanium tetrachloride ($TiCl_4$) as a precursor, sodium silicate as silica coating material and magnetite as magnetic cores [79]. This magnetised TiO_2 has been reported to remove approximately 60% of NOM in river water. However, the effectiveness of NOM removal by magnetised TiO_2 was still lower compared to single phase TiO_2. Therefore, the possibilities to develop a new magnetised 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_2, preparation/synthesis, characterisation and applications of magnetised TiO_2 for water purification. Generally, for about four decades, many studies have been carried out on titanium dioxide (TiO_2) as a photocatalyst for water purification; it is shown that TiO_2 is a promising material to solve water purification problems. However, the TiO_2 photocatalyst may causes difficulties during the separation phase from water. Therefore, the development of novel magnetised TiO_2 photocatalyst was carried out to overcome this problem, yet increase the reusability of photocatalyst particles. There are many studies of magnetised TiO_2 photocatalysts and, this paper is the first to review the field with a focus on water purification.

In the development of novel magnetised TiO_2, 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 were 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_2 shells onto silica-coated magnetite. It was due to expensive precursor was not required and this method yields highly photoactive TiO_2 coating at lower temperature. Moreover, in terms of commercialisation potential, this method may be preferred over sol–gel method in developing novel magnetised TiO_2.

Particle characterisation of magnetised TiO_2 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_2 and magnetised TiO_2 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, PCO treatment using TiO_2/UV system was used to remove a major contaminant in drinking water, namely NOM. A consolidated summary of photocatalytic degradation of organic contaminants using TiO_2 photocatalyst was shown at Table 6.

Recently, a cost-effective and practical method to prepare magnetised TiO_2 for NOM removal has been produced by using commercially viable raw materials, and this magnetised TiO_2 particle has been reported to remove approximately 60% of NOM in river water. However, the effectiveness of NOM removal by magnetised TiO_2 was still lower compared to single phase TiO_2. Therefore, the possibilities to develop a new magnetised TiO_2 photocatalyst, which is inexpensive and has high NOM removal properties, are considered for the future research.

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References

[1] J.-M. Herrmann, Heterogeneous photocatalysis: Fundamentals and applications to the removal of various types of aqueous pollutants, Catal. Today 53 (1999) 115–129.

[2] S. Parsons, Advanced Oxidation Processes for Water and Wastewater Treatment, IWA, London, 2004.

[3] B. Tansel, New technologies for water and wastewater treatment: A survey of recent patents, Recent Pat. Chem. Eng. 1 (2008) 17–26.

[4] R. Andreozzi, V. Caprio, A. Insola, R. Marotta, Advanced oxidation processes (AOP) for water purification and recovery, Catal. Today 53 (1999) 51–59.

[5] R.F. Howe, Recent developments in photocatalysis, Dev. Chem. Eng. Miner. Process. 6 (1998) 55–84.

[6] C. McCullagh, J. Robertson, D. Bahnemann, P. Robertson, The application of TiO_2 photocatalysis for disinfection of water contaminated with pathogenic micro-organisms: A review, Res. Chem. Intermed. 33 (2007) 359–375.

[7] S. Xuan, W. Jiang, X. Gong, Y. Hu, Z. Chen, Magnetically separable Fe_3O_4/TiO_2 hollow spheres: Fabrication and photocatalytic activity, J. Phys. Chem. C 113 (2008) 553–558.

[8] S. Chen, J. Li, K. Qian, W. Xu, Y. Lu, W. Huang, S. Yu, Large scale photochemical synthesis of $M@TiO_2$ nanocomposites (M = Ag, Pd, Au, Pt) and their optical properties, CO oxidation performance, and antibacterial effect, Nano Res. 3 (2010) 244–255.

[9] W.S. Tung, W.A. Daoud, New approach toward nanosized ferrous ferric oxide and Fe_3O_4-doped titanium dioxide photocatalysts, ACS Appl. Mat. Interfaces 1 (2009) 2453–2461.

[10] A. Fujishima, K. Honda, Electrochemical photolysis of water at a semiconductor electrode, Nature 238 (1972) 37–38.

[11] S. Watson, J. Scott, D. Beydoun, R. Amal, Studies on the preparation of magnetic photocatalysts, J. Nanopart. Res. 7 (2005) 691–705.

[12] S.U. Geissen, A. Weidemeyer, A. Vogelpohl, L. Bousselmi, A. Ghrab, A.E. Nnabi, Comparison of suspended and fixed photocatalytic reactor systems, Water Sci. Technol. 44 (2001) 245–249.

[13] D. Beydoun, R. Amal, J. Scott, G. Low, S. McEvoy, Studies on the Mineralization and separation efficiencies of a magnetic photocatalyst, Chem. Eng. Technol. 24 (2001) 745–748.

[14] D. Beydoun, R. Amal, G.K.C. Low, S. McEvoy, Novel photocatalyst: titania-coated magnetite. Activity and photodissolution, J. Phys. Chem. B 104 (2000) 4387–4396.

[15] H. de Lasa, B. Serrano, M. Salaices, in: H. Lasa, B. Serrano, M. Salaices, Photocatalytic Reaction Engineering, Springer, New York, NY, 2005, pp. 17–47.

[16] D. Tryk, A. Fujishima, K. Honda, Recent topics in photoelectrochemistry: Achievements and future prospects, Electrochim. Acta 45 (2000) 2363–2376.

[17] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Environmental applications of semiconductor photocatalysis, Chem. Rev. 95 (1995) 69–96.

[18] M.N. Rashed, A.A. El-Amin, Photocatalytic degradation of methyl orange in aqueous TiO_2 under different solar irradiation sources, Int. J. Phys. Sci. 2 (2007) 78–81.

[19] M. Noorjahan, M. Pratap Reddy, V. Durga Kumari, B. Lavédrine, P. Boule, M. Subrahmanyam, Photocatalytic degradation of H-acid over a novel TiO_2 thin film fixed bed reactor and in aqueous suspensions, J. Photochem. Photobiol. A: Chem. 156 (2003) 179–187.

[20] H.T. Chang, N.-M. Wu, F. Zhu, A kinetic model for photocatalytic degradation of organic contaminants in a thin-film TiO_2 catalyst, Water Res. 34 (2000) 407–416.

[21] M. Luo, D. Bowden, P. Brimblecombe, Removal of dyes from water using a TiO_2 photocatalyst supported on black sand, Water Air Soil Pollut. 198 (2009) 233–241.

[22] T.A. Gad-Allah, S. Kato, S. Satokawa, T. Kojima, Treatment of synthetic dyes wastewater utilizing a magnetically separable photocatalyst ($TiO_2/SiO_2/Fe_3O_4$): Parametric and kinetic studies, Desalination 244 (2009) 1–11.

[23] N.F. Zainudin, A.Z. Abdullah, A.R. Mohamed, Development of Supported TiO_2 Photocatalyst Based Adsorbent for Photocatalytic Degradation of Phenol, ICENV, Penang, 2008.

[24] S. Kwon, M. Fan, A.T. Cooper, H. Yang, Photocatalytic applications of micro-and nano-TiO_2 in environmental engineering, Crit. Rev. Environ. Sci. Technol. 38 (2008) 197–226.

[25] M. Samarghandi, J. Nouri, A. Mesdaghinia, A. Mahvi, S. Nasseri, F. Vaezi, Efficiency removal of phenol, lead and cadmium by means of $UV/TiO_2/H_2O_2$ processes, Int. J. Environ. Sci. Technol. 4 (2007) 19–25.

[26] D.C. Hurum, A.G. Agrios, K.A. Gray, T. Rajh, M.C. Thurnauer, Explaining the enhanced photocatalytic activity of degussa P25 mixed-phase TiO_2 using EPR, J. Phys. Chem. B 107 (2003) 4545–4549.

[27] S. Watson, D. Beydoun, R. Amal, Synthesis of a novel magnetic photocatalyst by direct deposition of nanosized TiO_2 crystals onto a magnetic core, J. Photochem. Photobiol. A: Chem. 148 (2002) 303–313.

[28] P. Thron, P. Pichat, C. Petrier, C. Guillard, Water treatment by TiO_2 photocatalysis and/or ultrasound: degradations of phenyltrifluoromethylketone, a trifluoroacetic-acid-forming pollutant, and octan-1-ol, a very hydrophobic pollutant, Water Sci. Technol. 44 (2001) 263–270.

[29] F. Chen, J. Zhao, Preparation and photocatalytic properties of a novel kind of loaded photocatalyst of $TiO_2/SiO_2/\gamma\text{-}Fe_2O_3$, Catal. Lett. 58 (1999) 246–247.

[30] T. Ohno, K. Sarukawa, K. Tokieda, M. Matsumura, Morphology of a TiO_2 photocatalyst (Degussa, P-25) consisting of anatase and rutile crystalline phases, J. Catal. 203 (2001) 82–86.

[31] S. Swetha, S.M. Santhosh, R. Geetha Balakrishna, Synthesis and comparative study of nano-TiO_2 over degussa P-25 in disinfection of water, Photochem. Photobiol. 86 (2010) 628–632.

[32] R.A. Al-Rasheed, Water treatment by heterogenous photocatalysis an overview, Presented at 4th SWCC Acquired Experience Symposium held in Jedda (2005).

[33] R.R. Bacsa, J. Kiwi, Effect of rutile phase on the photocatalytic properties of nanocrystalline titania during the degradation of p-coumaric acid, Appl. Catal. B: Environ. 16 (1998) 19–29.

[34] S. Sato, Photocatalytic activity of NOx-doped TiO_2 in the visible light region, Chem. Phys. Lett. 123 (1986) 126–128.

[35] W. Ren, Z. Ai, F. Jia, L. Zhang, X. Fan, Z. Zou, Low temperature preparation and visible light photocatalytic activity of mesoporous carbon-doped crystalline TiO_2, Appl. Catal. B: Environ. 69 (2007) 138–144.

[36] B. Tryba, Increase of the photocatalytic activity of TiO_2 by carbon and iron Modifications, Int. J. Photoenr. 2008 (2008) 1–15.

[37] T. Ohno, M. Akiyoshi, T. Umebayashi, K. Asai, T. Mitsui, M. Matsumura, Preparation of S-doped TiO_2 photocatalysts and their photocatalytic activities under visible light, Appl. Catal. A: Gen. 265 (2004) 115–121.

[38] A.J. Attia, S.H. Kadhim, F.H. Hussein, Photocatalytic degradation of textile dyeing wastewater using titanium dioxide and zinc oxide, E-J. Chem. 5 (2008) 219–223.

[39] U. Siemon, D. Bahnemann, J.J. Testa, D. Rodríguez, M.I. Litter, N. Bruno, Heterogeneous photocatalytic reactions comparing TiO_2 and Pt/TiO_2, J. Photochem. Photobiol. A: Chem. 148 (2002) 247–255.

[40] V. Vamathevan, R. Amal, D. Beydoun, G. Low, S. McEvoy, Silver metallisation of titania particles: Effects on photoactivity for the oxidation of organics, Chem. Eng. J. 98 (2004) 127–139.

[41] H. Chen, C. Deng, X. Zhang, Core–shell–shell magnetic microspheres for highly efficient enrichment of peptides and proteins for MALDI-ToF MS analysis, Angew. Chem. 122 (2010) 617–621.

[42] Q.-Y. Wen, D.-E. Gu, H.-W. Zhang, Q.-H. Yang, Y.-X. Li, Y.-L. Liu, J. Xiao, Magnetic properties of V-doped TiO_2 nanocrystalline film synthesized by liquid phase deposition technique, J. Phys. D: Appl. Phys. 42 (2009) 055012.

[43] B. Tural, N. Özkan, M. Volkan, Preparation and characterization of polymer coated superparamagnetic magnetite nanoparticle agglomerates, J. Phys. Chem. Solids 70 (2009) 860–866.

[44] Y.-H. Chen, Y.-Y. Liu, R.-H. Lin, F.-S. Yen, Photocatalytic degradation of p-phenylenediamine with TiO_2-coated magnetic PMMA microspheres in an aqueous solution, J. Hazard. Mater. 163 (2009) 973–981.

[45] Y. Li, M. Zhang, M. Guo, X. Wang, Preparation and properties of a nano TiO_2/Fe_3O_4 composite superparamagnetic photocatalyst, Rare Met. 28 (2009) 423–427.

[46] N.N. Hai, P. Van Vinh, Preparation and magnetic properties of TiO_2 doped with V, Mn, Co, La, J. Phys.: Conf. Ser., IOP Publishing, 2009, p. 012071.

[47] Y.-H. Chen, M. Franzreb, R.-H. Lin, L.-L. Chen, C.-Y. Chang, Y.-H. Yu, P.-C. Chiang, Platinum-doped TiO_2/magnetic poly (methyl methacrylate) microspheres as a novel photocatalyst, Ind. Eng. Chem. Res. 48 (2009) 7616–7623.

[48] B. Zhang, J. Zhang, F. Chen, Preparation and characterization of magnetic $TiO_2/ZnFe_2O_4$ photocatalysts by a sol–gel method, Res. Chem. Intermed. 34 (2008) 375–380.

[49] S.H. Xu, D.L. Feng, D.X. Li, W.F. Shangguan, Preparation of magnetic photocatalyst TiO_2 supported on $NiFe_2O_4$ and effect of magnetic carrier on photocatalytic activity, Chin. J. Chem. 26 (2008) 842–846.

[50] Q. He, Z. Zhang, J. Xiong, Y. Xiong, H. Xiao, A novel biomaterial: Fe_3O_4:TiO_2 core-shell nano particle with magnetic performance and high visible light photocatalytic activity, Opt. Mater. 31 (2008) 380–384.

[51] T.A. Gad-Allah, K. Fujimura, S. Kato, S. Satokawa, T. Kojima, Preparation and characterization of magnetically separable photocatalyst ($TiO_2/SiO_2/Fe_3O_4$): Effect of carbon coating and calcination temperature, J. Hazard. Mater. 154 (2008) 572–577.

[52] S. Xu, W. Shangguan, J. Yuan, M. Chen, J. Shi, Preparations and photocatalytic properties of magnetically separable nitrogen-doped TiO_2 supported on nickel ferrite, Appl. Catal. B: Environ. 71 (2007) 177–184.

[53] J.S. Nunes, C.L. de Vasconcelos, F.A.O. Cabral, J.H. de Araújo, M.R. Pereira, J.L.C. Fonseca, Synthesis and characterization of poly(ethyl methacrylate-co-methacrylic acid) magnetic particles via miniemulsion polymerization, Polymer 47 (2006) 7646–7652.

[54] S.A. Chambers, T.C. Droubay, T.C. Kaspar, Thin Films and Heterostructures for Oxide Electronics, Springer, New York, NY, 2005, pp. 219–247.

[55] M.-W. Xu, S.-J. Bao, X.-G. Zhang, Enhanced photocatalytic activity of magnetic TiO_2 photocatalyst by silver deposition, Mater. Lett. 59 (2005) 2194–2198.

[56] T. Fukumura, H. Toyosaki, Y. Yamada, Magnetic oxide semiconductors, Semicond. Sci. Technol. 20 (2005) S103.

[57] I.J. Bruce, J. Taylor, M. Todd, M.J. Davies, E. Borioni, C. Sangregorio, T. Sen, Synthesis, characterisation and application of silica-magnetite nanocomposites, J. Magn. Magn. Mater. 284 (2004) 145–160.

[58] D. Beydoun, R. Amal, Implications of heat treatment on the properties of a magnetic iron oxide–titanium dioxide photocatalyst, Mater. Sci. Eng.: B 94 (2002) 71–81.

[59] D. Beydoun, Development of a Novel Magnetic Photocatalyst: Preparation, Characterisation and Implication for Organic Degradation in Aqueous Systems, Sydney, School of Chemical Engineering and Industrial Chemistry, The University of New South Wales, Sydney, 2000.

[60] A.P. Philipse, M.P.B. van Bruggen, C. Pathmamanoharan, Magnetic silica dispersions: Preparation and stability of surface-modified silica particles with a magnetic core, Langmuir 10 (1994) 92–99.

[61] N. Buske, Application of magnetite sols in environmental technology, in: M. Schwuger, F. Haegel (Eds.), Surfactants and Colloids in the Environment, Springer, Berlin/Heidelberg, 1994, pp. 175–180.

[62] Y. Gao, B. Chen, H. Li, Y. Ma, Preparation and characterization of a magnetically separated photocatalyst and its catalytic properties, Mater. Chem. Phys. 80 (2003) 348–355.

[63] Y.S. Chung, S.B. Park, D.-W. Kang, Magnetically separable titania-coated nickel ferrite photocatalyst, Mater. Chem. Phys. 86 (2004) 375–381.

[64] W. Fu, H. Yang, M. Li, M. Li, N. Yang, G. Zou, Anatase TiO_2 nanolayer coating on cobalt ferrite nanoparticles for magnetic photocatalyst, Mater. Lett. 59 (2005) 3530–3534.

[65] F.A. Harraz, R.M. Mohamed, M.M. Rashad, Y.C. Wang, W. Sigmund, Magnetic nanocomposite based on titania–silica/cobalt ferrite for photocatalytic degradation of methylene blue dye, Ceram. Int. 40 (2014) 375–384.

[66] S.-W. Lee, J. Drwiega, D. Mazyck, C.-Y. Wu, W.M. Sigmund, Synthesis and characterization of hard magnetic composite photocatalyst—Barium ferrite/silica/titania, Mater. Chem. Phys. 96 (2006) 483–488.

[67] W. Fu, H. Yang, M. Li, L. Chang, Q. Yu, J. Xu, G. Zou, Preparation and photocatalytic characteristics of core-shell structure TiO_2/BaFe12O19 nanoparticles, Mater. Lett. 60 (2006) 2723–2727.

[68] H.-C. Huang, G.-L. Huang, H.-L. Chen, Y.-D. Lee, Immobilization of TiO_2 nanoparticles on Fe-filled carbon nanocapsules for photocatalytic applications, Thin Solid Films 515 (2006) 1033–1037.

[69] Y. Ao, J. Xu, D. Fu, C. Yuan, A simple route for the preparation of anatase titania-coated magnetic porous carbons with enhanced photocatalytic activity, Carbon 46 (2008) 596–603.

[70] D.H. Quiñones, A. Rey, P.M. Álvarez, F.J. Beltrán, P.K. Plucinski, Enhanced activity and reusability of TiO_2 loaded magnetic activated carbon for solar photocatalytic ozonation, Appl. Catal. B: Environ. 144 (2014) 96–106.

[71] S.-H. Wu, J.-L. Wu, S.-Y. Jia, Q.-W. Chang, H.-T. Ren, Y. Liu, Cobalt(II) phthalocyanine-sensitized hollow $Fe_3O_4@SiO_2@TiO_2$ hierarchical nanostructures: Fabrication and enhanced photocatalytic properties, Appl. Surf. Sci. 287 (2013) 389–396.

[72] H. Liu, S. Ji, Y. Zheng, M. Li, H. Yang, Porous TiO_2-coated magnetic core-shell nanocomposites: Preparation and enhanced photocatalytic activity, Chin. J. Chem. Eng. 21 (2013) 569–576.

[73] C.T. Fleaca, F. Dumitrache, I. Morjan, R. Alexandrescu, C. Luculescu, A. Niculescu, E. Vasile, V. Kuncser, Novel Fe@C–TiO_2 and Fe@C–SiO_2 water-dispersible magnetic nanocomposites, Appl. Surf. Sci. 278 (2013) 284–288.

[74] A. Abd Aziz, Y.H. Yau, G.L. Puma, C. Fischer, S. Ibrahim, S. Pichiah, Highly efficient magnetically separable TiO_2–graphene oxide supported $SrFe_{12}O_{19}$ for direct sunlight-driven photoactivity, Chem. Eng. J. 235 (2014) 264–274.

[75] Y. Yan, Z. Zheng, C. Deng, X. Zhang, P. Yang, Selective enrichment of phosphopeptides by titania nanoparticles coated magnetic carbon nanotubes, Talanta 118 (2014) 14–20.

[76] M. Fleet, The structure of magnetite, Acta Crystallogr. Sec. B 37 (1981) 917–920.

[77] J. Chen, W.H. Rulkens, H. Bruning, Photochemical elimination of phenols and COD in industrial wastewaters, Water Sci. Technol. 35 (1997) 231–238.

[78] S. Xu, W. Shangguan, J. Yuan, M. Chen, J. Shi, Preparation and photocatalytic properties of magnetically separable TiO_2 supported on nickel ferrite, Chin. J. Chem. Eng. 15 (2007) 190–195.

[79] S. Liu, Applications of Advanced Oxidation Processes for the treatment of Natural Organic Matter, School of Chemical Sciences and Engineering, The University of New South Wales, Sydney, 2009.

[80] S. Sakka, Handbook of Sol–gel Science and Technology. 1. Sol–gel Processing, Springer, New York, NY, 2005.

[81] H. Cheng, J. Ma, Z. Zhao, L. Qi, Hydrothermal preparation of uniform nanosize rutile and anatase particles, Chem. Mater. 7 (1995) 663–671.

[82] A.I. Kontos, I.M. Arabatzis, D.S. Tsoukleris, A.G. Kontos, M.C. Bernard, D.E. Petrakis, P. Falaras, Efficient photocatalysts by hydrothermal treatment of TiO_2, Catal. Today 101 (2005) 275–281.

[83] F.C. Mayville, R.E. Partch, E. Matijevic, Preparation of uniform spherical titania particles coated with polyurea by the aerosol technique, J. Colloid Interface Sci. 120 (1987) 135–139.

[84] M.S. Wooldridge, Gas-phase combustion synthesis of particles, Prog. Energy Combust. Sci. 24 (1998) 63–87.

[85] K.L. Choy, Chemical vapour deposition of coatings, Prog. Mater. Sci. 48 (2003) 57–170.

[86] Q. Powell, T. Kodas, B.M. Anderson, Coating of TiO_2 particles by chemical vapor deposition of SiO_2, Chem. Vap. Deposition 2 (1996) 179–181.

[87] L.N. Donselaar, A.P. Philipse, Interactions between silica colloids with magnetite cores: Diffusion, sedimentation and light scattering, J. Colloid Interface Sci. 212 (1999) 14–23.

[88] A.M. El-Toni, S. Yin, T. Sato, Control of silica shell thickness and microporosity of titania-silica core-shell type nanoparticles to depress the photocatalytic activity of titania, J. Colloid Interface Sci. 300 (2006) 123–130.

[89] Y. Liu, C. Ge, M. Ren, H. Yin, A. Wang, D. Zhang, C. Liu, J. Chen, H. Feng, H. Yao, T. Jiang, Effects of coating parameters on the morphology of SiO_2-coated TiO_2 and the pigmentary properties, Appl. Surf. Sci. 254 (2008) 2809–2819.

[90] Q. Liu, Z. Xu, J.A. Finch, R. Egerton, A novel two-step silica-coating process for engineering magnetic nanocomposites, Chem. Mater. 10 (1998) 3936–3940.

[91] P. Gherardi, E. Matijevic, Interactions of precipitated hematite with preformed colloidal titania dispersions, J. Colloid Interface Sci. 109 (1986) 57–68.

[92] R.C. Plaza, J.D.G. Durán, A. Quirantes, M.J. Ariza, A.V. Delgado, Surface chemical analysis and electrokinetic properties of spherical hematite particles coated with yttrium compounds, J. Colloid Interface Sci. 194 (1997) 398–407.

[93] I.U. Haq, E. Matijevic, Preparation and properties of uniform coated inorganic colloidal particles, J. Colloid Interface Sci. 192 (1997) 104–113.

[94] A. Hanprasopwattana, S. Srinivasan, A.G. Sault, A.K. Datye, Titania coatings on monodisperse silica spheres (characterization using 2-propanol dehydration and TEM), Langmuir 12 (1996) 3173–3179.

[95] B. Aiken, E. Matijevic, Preparation and properties of uniform coated inorganic colloidal particles. IV. Yttrium basic carbonate and yttrium oxide on hematite, J. Colloid Interface Sci. 126 (1988) 645–649.

[96] J. Li, H. Yu, Q. Sun, Y. Liu, Y. Cui, Y. Lu, Growth of TiO_2 coating on wood surface using controlled hydrothermal method at low temperatures, Appl. Surf. Sci. 256 (2010) 5046–5050.

[97] J.I. Taylor, C.D. Hurst, M.J. Davies, N. Sachsinger, I.J. Bruce, Application of magnetite and silica–magnetite composites to the isolation of genomic DNA, J. Chromatogr. A 890 (2000) 159–166.

[98] S. Watson, D. Beydoun, J. Scott, R. Amal, Preparation of nanosized crystalline TiO_2 particles at low temperature for photocatalysis, J. Nanopart. Res. 6 (2004) 193–207.

[99] S. Zhang, Z. Chen, Y. Li, Q. Wang, L. Wan, Y. You, Preparation of TiO_2 fibers by two-step synthesis method and their photocatalytic activity, Mater. Chem. Phys. 107 (2008) 1–5.

[100] K. Yanagisawa, J. Ovenstone, Crystallization of anatase from amorphous titania using the hydrothermal technique: effects of starting material and temperature, J. Phys. Chem. B 103 (1999) 7781–7787.

[101] M.Z. Dang, D.G. Rancourt, J.E. Dutrizac, G. Lamarche, R. Provencher, Interplay of surface conditions, particle size, stoichiometry, cell parameters, and magnetism in synthetic hematite-like materials, Hyperfine Interact. 117 (1998) 271–319.

[102] K. Yanagisawa, N. Yamasaki, Reduction of haematite to magnetite under controlled hydrothermal conditions with hydrogen gas, J. Mater. Sci. 26 (1991) 473–478.

[103] S. Liu, M. Lim, R. Amal, Magnetic Photocatalyst for Natural Organic Matter Oxidation, Chemeca 2008: Towards a Sustainable Australasia, 2008, p. 1785.

[104] S. Pavlova, I. Dobrevsky, Modified sirofloc process for natural water treatment, Desalination 173 (2005) 55–59.

[105] M. Semmens, M. Burckhardt, D. Schuler, P. Davich, M. Slunjski, M. Bourke, H. Nguyen, An evaluation of magnetic ion exchange (MIEX) For NOM removal, AWWA Annual Conference, Denver, CO, 2000, p. 5.8.

[106] J.P. Chen, L.K. Wang, L. Yang, S.-F. Lim, Emerging biosorption, adsorption, ion exchange, and membrane technologies, in: L.K. Wang, Y.-T. Hung, N.K. Shammas (Eds.), Advanced Physicochemical Treatment Technologies, Humana Press, Totowa, NJ, 2007, pp. 367–390.

[107] T. Matsunaga, R. Tomoda, T. Nakajima, H. Wake, Photoelectrochemical sterilization of microbial cells by semiconductor powders, FEMS Microbiol. Lett. 29 (1985) 211–214.

[108] B. Eikebrokk, T. Juhna, S. Osterhus, Water treatment by enhanced coagulation–operational status and optimization issues, TECHNEAU, Nieuwegein, Deliverable Number D 5 (2006).

[109] E. Pelizzetti, C. Minero, Mechanism of the photo-oxidative degradation of organic pollutants over TiO_2 particles, Electrochim. Acta 38 (1993) 47–55.

[110] U.I. Gaya, A.H. Abdullah, Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: A review of fundamentals, progress and problems, J. Photochem. Photobiol. A: Chem. Rev. 9 (2008) 1–12.

[111] D.F. Ollis, Contaminant degradation in water, Environ. Sci. Technol. 19 (1985) 480–484.

[112] M. Mrowetz, C. Pirola, E. Selli, Degradation of organic water pollutants through sonophotocatalysis in the presence of TiO_2, Ultrason. Sonochem. 10 (2003) 247–254.

[113] H. Harada, H. Tanaka, Sonophotocatalysis of oxalic acid solution, Ultrasonics 44 (2006) e385–e388.

[114] W. Chu, W.K. Choy, T.Y. So, The effect of solution pH and peroxide in the TiO_2-induced photocatalysis of chlorinated aniline, J. Hazard. Mater. 141 (2007) 86–91.

[115] R. Dillert, D. Bahnemann, H. Hidaka, Light-induced degradation of perfluorocarboxylic acids in the presence of titanium dioxide, Chemosphere 67 (2007) 785–792.

[116] H. Kim, W. Choi, Effects of surface fluorination of TiO_2 on photocatalytic oxidation of gaseous acetaldehyde, Appl. Catal., B 69 (2007) 127–132.

[117] Y. Ku, Y.-C. Lee, W.-Y. Wang, Photocatalytic decomposition of 2-chlorophenol in aqueous solution by UV/TiO_2 process with applied external bias voltage, J. Hazard. Mater. 138 (2006) 350–356.

[118] C. Guillard, J. Disdier, J.-M. Herrmann, C. Lehaut, T. Chopin, S. Malato, J. Blanco, Comparison of various titania samples of industrial origin in the solar photocatalytic detoxification of water containing 4-chlorophenol, Catal. Today 54 (1999) 217–228.

[119] T. Essam, M.A. Amin, O. El Tayeb, B. Mattiasson, B. Guieysse, Sequential photochemical–biological degradation of chlorophenols, Chemosphere 66 (2007) 2201–2209.

[120] M. Qamar, M. Saquib, M. Muneer, Semiconductor-mediated photocatalytic degradation of anazo dye, chrysoidine Y in aqueous suspensions, Desalination 171 (2005) 185–193.

[121] M. Faisal, M. Abu Tariq, M. Muneer, Photocatalysed degradation of two selected dyes in UV-irradiated aqueous suspensions of titania, Dyes Pigm. 72 (2007) 233–239.

[122] A. Danion, J. Disdier, C. Guillard, O. Païssé, N. Jaffrezic-Renault, Photocatalytic degradation of imidazolinone fungicide in TiO_2-coated optical fiber reactor, Appl. Catal. B: Environ. 62 (2006) 274–281.

[123] M.M. Haque, M. Muneer, Heterogeneous photocatalysed degradation of a herbicide derivative, isoproturon in aqueous suspension of titanium dioxide, J. Environ. Manage. 69 (2003) 169–176.

[124] C. Reyes, J. Fernández, J. Freer, M.A. Mondaca, C. Zaror, S. Malato, H.D. Mansilla, Degradation and inactivation of tetracycline by TiO_2 photocatalysis, J. Photochem. Photobiol. A: Chem. 184 (2006) 141–146.

[125] S. Horikoshi, H. Hidaka, N. Serpone, Photocatalyzed degradation of polymers in aqueous semiconductor suspensions, J. Photochem. Photobiol. A: Chem. 138 (2001) 69–77.

[126] M. Rashed, A. El-Amin, Photocatalytic degradation of methyl orange in aqueous TiO_2 under different solar irradiation sources, Int. J. Phys. Sci. 2 (2007) 73–81.

[127] D. Beydoun, R. Amal, G. Low, S. McEvoy, Role of nanoparticles in photocatalysis, J. Nanopart. Res. 1 (1999) 439–458.

[128] D. Mas, P. Pichat, C. Guillard, F. Luck, Removal of monochloroacetic acid in water by advanced oxidation based on ozonation in the presence of TiO_2 irradiated at $\lambda > 340$ nm, Ozone: Sci. Eng. 27 (2005) 311–316.

[129] H.K. Singh, M. Saquib, M.M. Haque, M. Muneer, D.W. Bahnemann, Titanium dioxide mediated photocatalysed degradation of phenoxyacetic acid and 2,4,5-trichlorophenoxyacetic acid, in aqueous suspensions, J. Molecular Catal. A: Chem. 264 (2007) 66–72.

[130] J. Gunlazuardi, W.A. Lindu, Photocatalytic degradation of pentachlorophenol in aqueous solution employing immobilized TiO_2 supported on titanium metal, J. Photochem. Photobiol. A: Chem. 173 (2005) 51–55.

[131] B. Bayarri, J. Giménez, D. Curcó, S. Esplugas, Photocatalytic degradation of 2,4-dichlorophenol by TiO_2/UV: Kinetics, actinometries and models, Catal. Today 101 (2005) 227–236.

[132] K. Selvam, M. Muruganandham, I. Muthuvel, M. Swaminathan, The influence of inorganic oxidants and metal ions on semiconductor sensitized photodegradation of 4-fluorophenol, Chem. Eng. J. 128 (2007) 51–57.

[133] Z. Zainal, L.K. Hui, M.Z. Hussein, Y.H. Taufiq-Yap, A.H. Abdullah, I. Ramli, Removal of dyes using immobilized titanium dioxide illuminated by fluorescent lamps, J. Hazard. Mater. 125 (2005) 113–120.

[134] M. Bertelli, E. Selli, Kinetic analysis on the combined use of photocatalysis, H_2O_2 photolysis, and sonolysis in the degradation of methyl tert-butyl ether, Appl. Catal. B: Environ. 52 (2004) 205–212.

[135] A.V. Vorontsov, E.N. Savinov, P.G. Smirniotis, Vibrofluidized- and fixed-bed photocatalytic reactors: Case of gaseous acetone photooxidation, Chem. Eng. Sci. 55 (2000) 5089–5098.

[136] V. Augugliaro, E. García-López, V. Loddo, S. Malato-Rodríguez, I. Maldonado, G. Marcì, R. Molinari, L. Palmisano, Degradation of lincomycin in aqueous medium: Coupling of solar photocatalysis and membrane separation, Solar Energy 79 (2005) 402–408.

[137] J. Peral, D.F. Ollis, Heterogeneous photocatalytic oxidation of gas-phase organics for air purification: Acetone, 1-butanol, butyraldehyde, formaldehyde, and m-xylene oxidation, J. Catal. 136 (1992) 554–565.

[138] M.A. Gondal, C. Li, X. Chang, L. Sikong, Z.H. Yamani, Q. Zhou, F. Yang, Q. Lin, Facile preparation of magnetic C/TiO_2/Ni composites and their photocatalytic performance for removal of a dye from water under UV light irradiation, J. Environ. Sci. Health, Part A 47 (2012) 570–576.

[139] R. Chalasani, S. Vasudevan, Cyclodextrin-functionalized Fe_3O_4@TiO_2: Reusable, magnetic nanoparticles for photocatalytic degradation of endocrine-disrupting chemicals in water supplies, ACS Nano 7 (2013) 4093–4104.

[140] L. Erdei, N. Arecrachakul, S. Vigneswaran, A combined photocatalytic slurry reactor–immersed membrane module system for advanced wastewater treatment, Sep. Purif. Technol. 62 (2008) 382–388.