SYNTHESIS AND CHARACTERIZATION OF TITANIUM DIOXIDE NANOTUBES FOR SONOCATALYTIC DEGRADATION OF ORGANIC DYES IN WASTEWATER

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by

PANG YEAN LING

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LIST OF ABBREVIATIONS

Symbol	Description
a. u.	Arbitrary unit
AAS	Atomic absorption flame emission spectroscopy
AF	Azo fuchsine
ANOVA	Analysis of variance
AOPs	Advanced oxidation processes
ARB	Acid Red B
at.	Atomic percentage
BB 41	Basic Blue 41
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
BOD	Biochemical oxygen demand
CCD	Central composite design
CMP	2-chloro-5-methyl phenol
COD	Chemical oxygen demand
DoE	Design of experiment
EA	Elemental analysis
EDX	Energy dispersive X-ray
e.g.	For example
1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
FT-IR	Fourier transformed infrared spectroscopy

GC/MS	Gas chromatograph coupled with mass spectrometry
HPLC	High performance liquid chromatography
i.e.	That is
IUPAC	International Union of Pure and Applied Chemistry
LC/MS	Liquid chromatograph method coupled with mass spectroscope
MB	Methylene Blue
MO	Methyl Orange
MP	Methyl parathion
n.d.	No data
NPs	Nanoparticles
NTs	Nanotubes
P	Product/ intermediate product
Prob >*F*	Probability of seeing the observed *F* value if the null hypothesis is true
pzc	Point of zero charge
RB5	Reactive Black 5
RSM	Response surface methodology
S	Substrate
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TGA-DTA	Thermal gravimetric analysis-differential thermal analysis
TOC	Total organic carbon
UV	Ultraviolet
UV-vis DRS	UV-vis diffuse reflectance spectroscopy
wt.	Weight percentage

XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy

LIST OF SYMBOLS

Symbols	Descriptions	Unit
α	The distance of the axial point from center point in CCD	Dimensionless
α_a	Absorption coefficient of the semiconductor material	(m^{-1})
A	Arrhenius factor (pre-exponential factor)	Dimensionless
A_a	Absorption constant of the semiconductor material	(m^{-1})
β	Full width at half maximum of selected peak	Radians
β_o, β_i, β_{ii} *and* β_{ij}	Constant, linear, quadratic and interaction coefficients	Dimensionless
c	Velocity of light	(m/s)
C_0	Initial concentration of organic pollutant	(mg/L)
C_t	Concentration of dye at time, *t*	(mg/L)
$-\frac{dC}{dt}$	Differential of concentration of organic pollutant with respect to time (*t*)	(mg/L.min)
D	Dye molecule	Dimensionless
D_c	Average size of crystallite	(m)
e^-	Electron	Dimensionless
E_a	Activation energy	(kJ/mol)
E_g	Band gap energy	(eV)
ε	Standard error	Dimensionless
F-value	Ratio of model mean square to residuals mean square	Dimensionless
γ	Specific heat ratio of the gas/vapor mixture	Dimensionless
h	Planck constant	eVs

h^+	Hole	Dimensionless
$h\nu$	Photon energy	(eV)
I_A	Intensity of anatase reflection	(Counts/s)
I_R	Intensity of rutile reflection	(Counts/s)
k	Apparent reaction rate constant used in the Langmuir-Hinshelwood model	(mg/L.min)
k'	Rate constant for oxidation Rhodamine B by •OH	(min^{-1})
K	Equilibrium constant	(L/mg)
k_1	Rate constant of adsorption of organic pollutant from the bulk solution to the interfacial region of cavitation bubbles	(min^{-1})
k_{-1}	Rate constant of desorption of organic pollutant from the bulk solution to the interfacial region of cavitation bubbles	(mg/L.min)
k_{app}	Apparent reaction rate constant in the different reaction order models	(mg/L.min or min^{-1} or L/mg.min for zero, first and second order)
k_D and k'_D	Forward and backward rate constant of adsorption and desorption of dye	(min^{-1})
k_e	Rate constant of sonolytic catalyst	(min^{-1})
k_{hci}	Rate constants for oxidation dye by hole, i = 1 and 2	(min^{-1})
k_{hf} and k_{hb}	Forward and backward rate constants of recombination •OH to form H_2O_2	(min^{-1})
k_{OH} and k'_{OH}	Forward and backward rate constant of adsorption of •OH	(min^{-1})
k_{oxi}	Rate constants for oxidation dye by •OH (presence of catalyst), i = 1,2,3 and 4	(min^{-1})
k_p	Rate constant of sonolysis water	(min^{-1})

k_{rc}	Rate constant of recombination hole and electron to generate heat	(min^{-1})
k_{rh1}	Rate constant of adsorbed •OH species oxidized by hole	(min^{-1})
k_{rh2}	Rate constant of adsorbed H_2O species oxidized by hole	(min^{-1})
k_{s1}, k_{s2} *and* k_{s3}	Rate constants for side reactions to form free radicals	(min^{-1})
λ	Wavelength of the light	(nm)
λ_x	Wavelength of the X-ray	(nm)
n	Number	Dimensionless
P	Pressure	(bar)
P_a	Pressure in the liquid (a sum of the hydrostatic and acoustic pressures)	(bar)
P_H	Hydrostatic pressure	(atm)
P_v	Pressure inside the bubble at its maximum size or the vapour pressure of the liquid	(bar)
P/P_0	Relative pressure	Dimensionless
ρ_L	Density of liquid	(kg/m^3)
r	Reaction rate of organic pollutant	(mg/L.min)
r_1	Rate of adsorption of the organic pollutant from the bulk solution to the interfacial region of cavitation bubbles	(mg/L.min)
r_{-1}	Rate of desorption of the organic pollutant from the interfacial region of cavitation bubbles to the bulk solution	(mg/L.min)
r_D	Reaction rate of dye	(mg/L.min)
R^2	Coefficient of determination	Dimensionless
R^2_{adj}	Adjusted coefficient of determination	Dimensionless
R_g	Universal gas constant	(J/mol.K)

R_m	Maximum radius of cavitation bubbles	(m)
R_{max}, R_{min} and R	Maximum reflectance, minimum reflectance and the reflectance at any intermediate photon energy	Dimensionless
S_c	Surface of catalyst	Dimensionless
T	Reaction temperature	(K)
T_{max}	Maximum temperature developed in the cavitation bubbles	(K)
T_0	Temperature of the bulk solution	(K)
T_p	Ultrasonic period	(s)
t	Irradiation time	(min)
t_t	Thickness of the semiconductor material	(m)
τ	Cavitation bubbles collapse time	(s)
W_A	Weight fraction of anatase	(%)
W_R	Weight fraction of rutile	(%)
x_i *and* x_j	Independent process variables, i = 1,2 and 3	Depands
y	Response of the degradation process	(%)
θ	Diffraction angle	Degree (^{o})
θ_n	Ratio of the number of adsorbed organic pollutant molecules in the interfacial region to the maximum number of the adsorbable organic pollutant molecules	Dimensionless

SINTESIS DAN PENCIRIAN NANOTIUB TITANIUM DIOKSIDA BAGI PENGURAIAN SONO BERMANGKIN PENCELUP ORGANIK DALAM AIR SISA

ABSTRAK

Penguraian sono bermangkin bagi Rhodamin B telah dikaji menggunakan nanotiub titanium dioksida (NTs TiO_2) yang berbeza dengan pengolahan suhu dari 300 ^{o}C hingga 900 ^{o}C dengan tempoh masa 2 jam. Pencirian mangkin telah dikaji dengan menggunakan SEM, TEM, EDX, EA, AAS, XRD, spektroskopi Raman, FT-IR, penjerapan-penyahjerapan nitrogen, UV-vis DRS, TGA-DTA, pengukuran keupayaan Zeta dan XPS. Kesan terhadap aktiviti sono bermangkin dengan menggunakan nanopartikel TiO_2 atau pelbagai tersepuh NTs TiO_2 dan pelbagai parameter ujikaji termasuk pengunaan pelbagai pencelup organik (Congo Merah, Reaktif Biru 4, Metil Jingga, Metilena Biru dan Rhodamin B), kepekatan asal Rhodamin B 50–150 mg/L, dos mangkin 0.5–2.5 g/L, pH larutan 1–11, frekuensi ultrasonik 35 atau 130 kHz, kuasa ultrasonik 20–100 W, dos hidrogen peroksida (H_2O_2) 4–20 mM, suhu larutan 25–50 ^{o}C dan kewujudan udara terlarut telah diselidik untuk menentukan keadaan optimum. Keadaan optimum bagi penguraian sono bermangkin bagi Rhodamin B yang tertinggi (88.47 % selepas 2 jam) berlaku apabila 50 mg/L kepekatan asal Rhodamin B, 2 g/L dosej mangkin, pH larutan 7, frekuensi ultrasonik 35 kHz, kuasa ultrasonik 50 W dan 8 mM dosej H_2O_2 pada 45 ^{o}C ± 2 digunakan. NTs TiO_2 yang sedia ada diubahsuai dengan memperkenalkan urea kepada NTs TiO_2 pada nisbah molar N: Ti di antara 0.1–1.0. Pendopan urea pada N: Ti sama dengan 0.3 mangakibatkan kenaikan penguraian sono bermangkin bagi Rhodamin B kepada 86.75 % selepas 1 jam. Sementara itu, Fe-didopkan NTs TiO_2 pada nisbah molar Fe: Ti di antara 0.001–0.02 telah disediakan. Optimum Fe pendopan pada Fe: Ti sama dengan 0.005 menunjukkan keaktifan penguraian sono bermangkin yang tertinggi (91.19 %) selepas 1 jam. Dipercayai bahawa pendopan logam dan bukan logam boleh menggalakkan luas permukaan tertentu yang besar, tenaga jalur luang yang rendah, permukaan kekosongan oksigen yang banyak dan aktif, bererti membaiki keaktifan sono bermangkin NTs TiO_2. Fe^{3+} yang dilarutkan boleh memangkin tindak balas serupa Fenton yang selanjutnya membaiki tindak balas penguraian sono bermangkin. Penguraian sono bermangkin bagi Rhodamin B mengikuti kinetik tertib pertama yang ketara dan tindak balas tersebut hampir mematuhi persamaan keserupaan model kinetik Langmuir-Hinshelwood. Kajian penggunaan mangkin semula menunjukkan bahawa pengurangan aktiviti mangkin, Fe-didopkan NTs TiO_2 adalah dalam 6.58 % selama empat kitaran berturut-turut dengan kehilangan Fe daripada permukaan mangkin yang minimum. Penguraian sono bermangkin bagi air sisa tekstil sebenar yang menggunakan Fe-didopkan NTs TiO_2 pada Fe: Ti sama dengan 0.005 telah diselidiki. Kecekapan penguraian yang terbaik boleh dicapai pada pH larutan 3, 6 g/L dosej mangkin, 40 mM dosej H_2O_2, frekuensi ultrasonik 35 kHz dan kuasa ultrasonik 50 W selepas 1 jam masa penjerapan diikuti dengan 3 jam masa penyinaran ultrasonik di bawah udara terlarut yang berterusan. Penyingkiran warna, COD and TOC masing-masing ialah 79.9 %, 59.4 % and 49.8 %.

SYNTHESIS AND CHARACTERIZATION OF TITANIUM DIOXIDE NANOTUBES FOR SONOCATALYTIC DEGRADATION OF ORGANIC DYES IN WASTEWATER

ABSTRACT

The sonocatalytic degradation of Rhodamine B was studied using titanium dioxide nanotubes (TiO_2 NTs) with various annealing temperatures ranging from 300 ^{o}C to 900 ^{o}C for 2 h. Characterizations of the catalysts were performed using SEM, TEM, EDX, EA, AAS, XRD, Raman spectroscopy, FT-IR, nitrogen adsorption-desorption, UV-vis DRS, TGA-DTA, zeta potential measurement and XPS. The effect of catalytic activity for TiO_2 nanoparticles (NPs) or various annealed TiO_2 NTs and various experimental parameters including the use of various organic dyes (Congo Red, Reactive Blue 4, Methyl Orange, Methylene Blue and Rhodamine B), initial concentration of Rhodamine B of 50–150 mg/L, catalyst dosage of 0.5–2.5 g/L, solution pH of 1–11, ultrasonic frequency of 35 or 130 kHz, ultrasonic power of 20–100 W, hydrogen peroxide (H_2O_2) dosage of 4–20 mM, solution temperature of 25–50 ^{o}C and the presence of dissolved air at 1 L/min were examined to determine the optimum conditions. The optimum conditions for sonocatalytic degradation of Rhodamine B (88.47 % after 2 h) occurred when the initial concentration of the dye was 50 mg/L, 2 g/L of TiO_2 NTs-300, solution pH of 7, ultrasonic power of 50 W, ultrasonic frequency of 35 kHz and H_2O_2 dosage was 8 mM at 45 $^{o}C \pm 2$. The as-prepared TiO_2 NTs was modified by introducing urea on TiO_2 NTs at molar ratios of N: Ti between 0.1–1.0. Urea doping at N: Ti equals to 0.3 led to an increment in the sonocatalytic degradation of Rhodamine B up to 86.75 % after 1 h. Meanwhile, Fe-doped TiO_2 NTs at molar ratios of Fe: Ti between 0.001–0.02 were prepared. Fe doping at Fe: Ti equals to 0.005 gave the highest sonocatalytic activity (91.19 %) after 1 h. It was believed that metal or non-metal doping could induce higher specific

surface areas, lower band gap energy, more active surface oxygen vacancies which significantly improved sonocatalytic activity. Leached Fe^{3+} could catalyze Fenton-like reaction to further improve the sonocatalytic reaction. The sonocatalytic degradation Rhodamine B followed apparent first-order kinetic reaction and the reaction was well fitted using an equation similar to Langmuir-Hinshelwood kinetic model. Catalyst reusability study revealed that the reduction in catalytic activity for Fe-doped TiO_2 NTs was within 6.58 % for the four successive cycles with minimum loss of Fe from the catalyst surface. The sonocatalytic degradation of real textile wastewater in the presence of Fe-doped TiO_2 NTs at Fe: Ti equals to 0.005 was also investigated. The best degradation was achieved at a solution pH of 3, 6 g/L of catalyst dosage, 40 mM of H_2O_2, an ultrasonic frequency of 35 kHz and an output power of 50 W after 1 h of adsorption followed by 3 h of ultrasonic irradiation under continuous dissolved air conditions. The color, COD and TOC removals were 79.9 %, 59.4 % and 49.8 %, respectively.

CHAPTER 1

INTRODUCTION

1.1. Water pollution in Malaysia

The problem of water pollution in Malaysia has been receiving increased attention. Figure 1.1 shows the decreasing number of clean rivers and an increase in the number of polluted rivers throughout 2006 to 2011. According to Malaysia Environment Quality Report (Department of Environment, 2011), the increasing number of cases of water pollution was due to the increasing sewage treatment plants and manufacturing industries. Among the industrial sources of water pollution, textile finishing wastewater accounts for 22 % of the total volume of industrial wastewater generated in Malaysia (Rakmi, 1993). Before 1993, biological processes were generally preferable for wastewater treatment due to the low cost and less usage of chemical reagents.

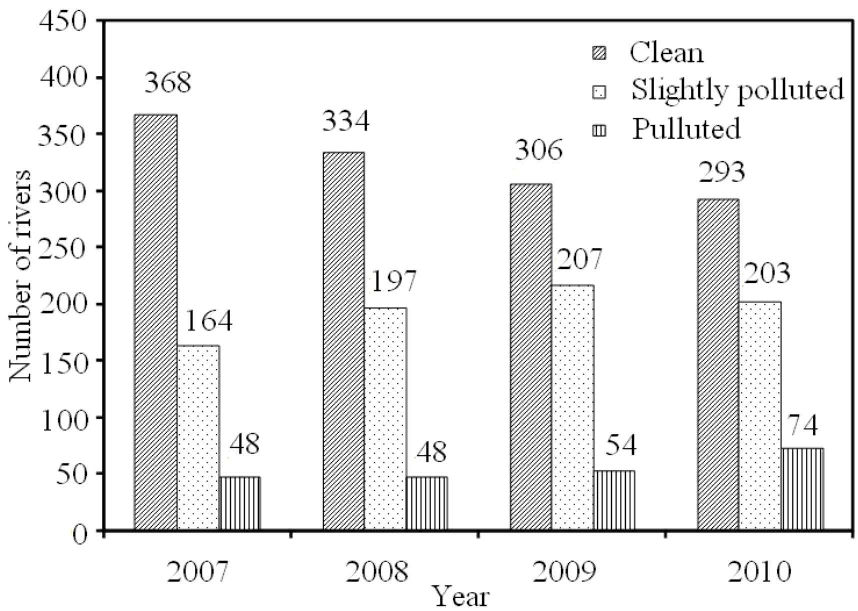


Figure 1.1: River water quality trend in Malaysia between 2007−2011 (Department of Environment, 2011).

1.2 Dye production, characteristics of textile industry effluent and its environmental impacts

Until recently, there is no data available on the exact amount of annual production of organic dyes in the world. However, more than 100,000 types of commercially available dyes exist and an annual worldwide production of synthetic dyes of nearly 1 million tons has been reported in the literature (Sinha *et al.*, 2013). An estimated 90 % of the total dyes production will end up in fabrics, while the remaining portion of the dyes will be used in leather, paper, plastic and chemical industries (Hameed *et al.*, 2007). It is estimated that 280,000 tons of textile dyes is discharged as industrial effluent every year worldwide (Ali, 2010).

The typical characteristics of wastewater from the effluents of the dyeing and finishing processes are shown in Table 1.1. It also shows the discharge quality standards which are stipulated in the Environmental Quality (Sewage Industrial Effluent) Regulations, 2009 to comply with the minimum requirements of the Environmental Quality Act 1974 (Department of Environment, 2011). Results in Table 1.1 show a range of values for each parameter involved which suggest a large variability of the wastewater quality from the dyeing and finishing processes.

The release of the persistent dyes structure with toxicity properties may cause negative impacts or hazards to human health and the ecosystem. The non-biodegradable nature of organic dyes and their high colour intensity are able to reduce aquatic diversity by blocking the passage of sunlight through the water (Jibril *et al.*, 2013). Moreover, some of them are capable of causing irritations to the skin, eyes, allergic dermatitis and respiratory tract (Merouani *et al.*, 2010b). The presence of azo- and nitro-compounds in the structure of organic dyes has the possibility to generate aromatic amines if the textile effluent is incompletely treated. Aromatic amines are toxic, carcinogenic and mutagenic, so that some are capable of inducing cancer and tumor in human (Sun *et al.*, 2013).

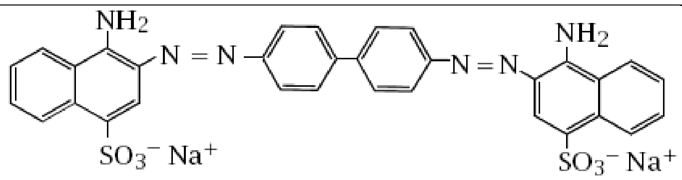
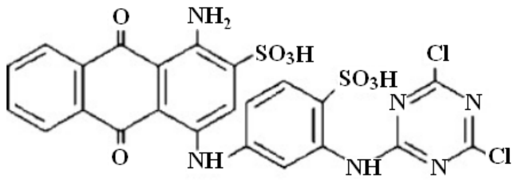
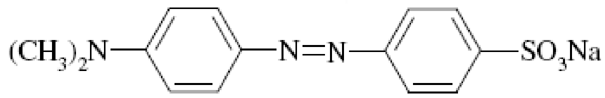
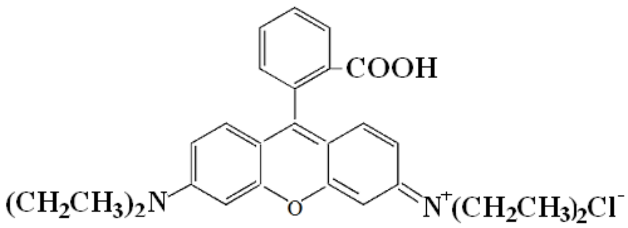
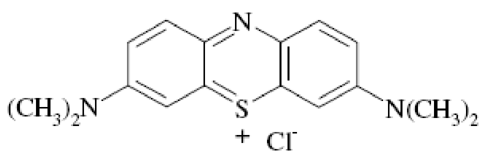
Table 1.1: Typical characteristics of wastewater from a textile dyeing process and maximum effluent parameter limits for Standards A and B.

Parameters / component	Typical values	Standard A	Standard B	References
Temperature (^oC)	30–80	40	40	(Lau and Ismail, 2009)
pH	2–10	6.0–9.0	5.5–9.0	(Verma *et al.*, 2012)
Biochemical oxygen demand (BOD_5) (mg/L)	110–5,600	20	50	(Verma *et al.*, 2012)
Chemical oxygen demand (COD) (mg/L)	2–5 x BOD_5	50	100	(Kaushik and Malik, 2009)
Total suspended solids (mg/L)	50–23,950	50	100	(Verma *et al.*, 2012)
Chromium				
hexalent (mg/L)	0.35–	0.05	0.05	(Kaushik and Malik,
trivalent (mg/L)	170	0.20	1.0	2009)
Copper (mg/L)	0.12–4.20	0.20	1.0	(Kaushik and Malik, 2009)
Nickel (mg/L)	0.10–0.96	0.20	1.0	(Kaushik and Malik, 2009)
Zinc (mg/L)	0.10–58	1.0	1.0	(Kaushik and Malik, 2009)
Phosphorous (mg/L)	0.3–15	n.d.	n.d.	(Lau and Ismail, 2009)
Nitrite (NO_2^-) (mg/L)	0.2–28	0.4	1.0	(Vilar *et al.*, 2011)
Nitrate (NO_3^-) (mg/L)	7–74	7.0	10.0	(Saeed and Sun, 2013)
Colour (Pt/Co)	> 300	*	*	(Lau and Ismail, 2009)

*The liquid effluent should not be coloured.
Standard A for discharge upstream of drinking water take-off.
Standard B for inland waters.

Five types of dye are investigated in this research work as shown in Table 1.2. The Ecological and Toxicological Association of the Dyestuffs Manufacturing Industry in year 1974 found that basic dyes and diazo direct dyes have the highest toxicity among 4000 dyes tested (Robinson *et al.*, 2001). It is reported that basic dyes have high brilliance and colour intensity even in a very low concentration (Merouani *et al.*, 2010b). **One of** the main organic dyes used as a model pollutant in many studies is Rhodamine B. Meanwhile, acid and reactive dyes with azo or anthraquinone group are toxic to some organisms and may cause direct destruction on many creatures in water (Ahmad and Hameed, 2010).

Table 1.2: Chemical structures and classifications of organic dyes used in this study (Tangestaninejad *et al.*, 2008; Jamalluddin and Abdullah, 2011).

Dyes	Classification	Chemical structure
Congo Red	Anionic direct diazo	
Reactive Blue 4	Anionic reactive anthraquinone	
Methyl Orange	Anionic acid monoazo	
Rhodamine B	Cationic basic xanthene	
Methylene Blue	Cationic basic thiazine	

1.3 Colour removal techniques

The presence of dyes in wastewater effluent is highly undesirable. As such, several treatment methods which include physical, chemical and biological treatments have been applied before discharge to the environment. Some of the dye conventional removal techniques with their respective limitations in textile industry have been discussed. Adsorption using commercially available activated carbon is very expensive and the need of regeneration becomes its limitation to be widely used. Thus, many efforts have been made to search for lower cost waste material adsorbents such as bamboo waste (Ahmad and Hameed, 2010), rejected tea (Nasuha and Hameed, 2011), coffee residues (Kyzas *et al.*, 2012), waste newspaper (Zhang *et al.*, 2013), oil palm empty fruit bunch (Sajab *et al.*, 2013) and pineapple peel (Foo and Hameed, 2012). Adsorption may be effective for decolourization but the process only involves a phase transfer of pollutants to other secondary wastes that subsequently require additional treatment or proper disposal procedure.

Filtration technology to treat textile effluents includes microfiltration (Baburaj *et al.*, 2012), ultrafiltration (Aouni *et al.*, 2012), nanofiltration (Ellouze *et al.*, 2012; Shao *et al.*, 2013; Zheng *et al.*, 2013) and reverse osmosis (Liu *et al.*, 2011; Kurt *et al.*, 2012). However, the disadvantages of this method are such as it can only be applied on small wastewater flow rate, high cost of membrane formation, high working pressure to push the wastewater flow through membrane filtration and inability to reduce dissolved solid content. Thus, this method requires frequent cleaning and replacement of the modules to maintain effectiveness in removing of organic dyes.

Biodegradation of organic dyes is very difficult as the structure of organic dyes is usually very complex, stable and sometimes it contains long-lasting colourants. Nevertheless, the possible microorganisms used for biodegradation dyes are fungi (Lade *et al.*, 2012), bacteria (Cui *et al.*, 2012), yeasts (Qu *et al.*, 2012) and algae (Daneshvar *et al.*, 2012; Baldev *et al.*, 2013). The problems which limit their application in industry are the toxicity of dyes toward the organisms used in the aerobic biological process and long hydraulic retention time so that larger tank is generally required. On the other hand, the main problem which occurs in colour removal under anaerobic condition is the production of aromatic amine during azoreductase cleavage of the azo bond which is more toxic than the dye itself (Qu *et al.*, 2012).

Chemical treatment includes coagulation and flocculation using aluminium sulfate, lime and ferric salts (Verma *et al.*, 2012). However, the handling of large volume of concentrated sludge produced would increase the capital cost for wastewater treatment. Other limitations that need to be considered for this technique are the high cost of coagulating or flocculating agent and the pH dependency for effective dye removal. Meanwhile, ion exchange method is ineffective to remove several types of dye simultaneously. Both cationic (basic dyes) and anionic (acid, direct, reactive dyes) types can only be removed effectively using different resins (Makhoukhi *et al.*, 2010; Wawrzkiewicz, 2012; Wawrzkiewicz, 2013). Other disadvantages are such as low removal in the case of nonionic dyes (disperse dyes), diffusion limitation that can affect reaction rate while the use of organic solvent for regeneration is very expensive (Robinson *et al.*, 2001).

Chemical oxidation for complete mineralization is a focus area in advanced oxidation processes (AOPs). Fenton and Fenton-like treatments have been reported for the ability to decolourize a wide range of textile dyes in rather short reaction times (Zhu *et al.*, 2012). The major disadvantage of this method is sludge generation through the flocculation of the reagent and the dye molecules. Ozonation of textile effluents results in efficient colour removal, enhanced biodegradability and reduction in non-biodegradable COD (Oller *et al.*, 2011). Ozonation can rapidly decolourize water-soluble dyes but takes a longer time to oxidize non-soluble dyes (van der Zee, 2002). It also has a relatively short life time of approximately 20 min (Buntat *et al.*, 2009).

On the other hand, photocatalytic and sonocatalytic processes are able to mineralize dye molecules to carbon dioxide (CO_2) and water (H_2O). Both types of degradation rate can be enhanced by adding hydrogen peroxide (H_2O_2) to increase the formation of hydroxyl radical (•OH). •OH has become an important oxidant due to its high reactivity and lack of selectivity towards organic compounds. The disadvantage of the photocatalytic process is the low penetration ability (several millimeters) in water medium. However, higher penetrating ability (25–30 cm) in water medium can be achieved through the use of ultrasonic irradiation (Zhang and Oh, 2010). Hence, there has been an increase of interest in the use of ultrasound to destroy organic contaminants that present in wastewater.

1.4 Problem statement

The main issue faced by textile industry is the incomplete degree of fixation of dyes that leads to water pollution during textile fiber processing. Most of these organic dyes can cause irritation to the skin, eyes and systemic effects including blood changes, gastrointestinal tract and respiratory tract. Besides, the presence of benzene ring in the dye structure always causes conventional treatment process to be ineffective in destroying the organic pollutants (Wang *et al.*, 2007a). Therefore, the most promising way is the application of AOPs to oxidize those hazardous organic pollutants. Among AOPs, photocatalytic degradation is a plausible method but it has limited practical application in treating heavily coloured effluents due to low penetration of the ultraviolent (UV) light. Hence, the application of ultrasonic irradiation could overcome the main drawbacks of UV light.

However, the successful application of titanium dioxide (TiO_2) is still constrained by the wide band gap energies (3.2 or 3.0 eV in the anatase or rutile phase, respectively) (Wang *et al.*, 2008b). Most of the research works done so far do not address the optimum conditions for sonocatalytic degradation of dye. Optimization of sonocatalytic degradation of dyes using response surface methodology is rarely reported. In addition, reaction kinetic for sonocatalytic degradation of dye is yet to be well established. The activity of TiO_2 is known to decrease dramatically for the reapplication in the sonocatalytic or photocatalytic degradation. Lastly, information on the sonocatalytic treatment for real textile wastewater is quite scarce as most of the research works done are merely limited to the removal of specific dyes from pure dye solutions.

Therefore, TiO_2 nanotubes (NTs) catalyst is prepared by hydrothermal treatment before treating the organic dye in aqueous solution under ultrasonic irradiation. Besides, TiO_2 NTs have improved properties as compared to TiO_2 NPs such as high aspect ratio that can result in higher surface area. Then, different effects of operating parameters on the sonocatalytic degradation of dye in the presence of TiO_2 NTs are worth investigation and elucidation. Optimum conditions and interaction effects between parameters to achieve higher efficiency of sonocatalytic degradation of the dye should be identified. The purposes of introducing iron or nitrogen ions into TiO_2 NTs are to narrow the band gap energy of TiO_2 NTs and to increase the transport of separated electron throughout the nanotubes. The catalytic activity and stability of catalyst developed during ultrasonic irradiation should also be evaluated. A reliable reaction kinetic for degradation of dye needs to be proposed. Lastly, the feasibility of oxidative decolourization of textile wastewater through adsorption followed by ultrasonic irradiation in the presence of Fe-doped TiO_2 NTs should be evaluated.

1.5 Research objectives

The main goal of this study is to develop a novel TiO_2 catalyst as a sonocatalyst for repeated usage in sonocatalytic degradation of dyes without suffering from significant activity decrease. Specific objectives of this study include the following:

i. To synthesize and characterize TiO_2 NTs using hydrothermal synthesis and annealing with different temperatures in order to accelerate the sonocatalytic degradation reaction of Rhodamine B in water.

ii. To demonstrate the process behaviour of the sonocatalytic degradation process under various operating conditions with the objective of identifying the most suitable and optimum reaction conditions.

iii. To study the characteristics of doped TiO_2 NTs by incorporating nitrogen at molar ratios of N: Ti between 0.1–1.0 or iron ions at molar ratios of Fe: Ti between 0.001–0.02 in order to enhance the sonocatalytic activity.

iv. To study the reusability of the un-doped and Fe-doped TiO_2 NTs covering the evaluation of the sonocatalytic activity during repeated use and its stability after ultrasonic irradiation through various suitable characterization methods.

v. To study the reaction kinetic orders, Langmuir-Hinshelwood kinetic to model the sonocatalytic degradation process and performance of sonocatalytic degradation using real textile industry wastewater.

1.6 Research scope

TiO_2 NTs was synthesized through a hydrothermal method in a concentrated alkali solution. Effects of various heat treatments (300 ^oC, 500 ^oC, 700 ^oC and 900 ^oC) on the characteristics of the TiO_2 NTs sonocatalysts and their consequent effects on the catalytic activity were investigated. TiO_2 NPs and TiO_2 NTs were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray (EDX) analysis, X-ray diffraction (XRD), Raman spectroscopy, Fourier transformed infrared (FT-IR) spectroscopy, nitrogen adsorption-desorption isotherm, UV-vis diffuse reflectance spectroscopy (UV-vis DRS), thermal gravimetric analysis-differential thermal analysis (TGA-DTA) and zeta potential measurements.

Then, a series of experiments were conducted using TiO_2 NPs and different types of heat-treated TiO_2 NTs catalysts to compare the degradation performance of Rhodamine B. This is followed by sonolytic and sonocatalytic degradation of various organic dyes including Congo Red, Reactive Blue 4, Methyl Orange, Methylene Blue and Rhodamine B. The process variables investigated include the effect of initial concentration of Rhodamine B (50–150 mg/L), the effect of catalyst dosage (0.5–2.5 g/L), the effect of solution pH (pH 1–pH 11), the effect of ultrasonic frequency (35 kHz or 130 kHz), the effect of ultrasonic power (20–100 W), the effect of solution temperature (25 ^{o}C–50 ^{o}C), the effect of H_2O_2 dosage (4–20 mM) and finally the effect of the presence of dissolved air at 1 L/min. Each of the range of variables chosen was based on reports in the literature and through the process of trial and error during preliminary study. Besides, the optimum conditions of three process variables for the sonocatalytic degradation of Rhodamine B were obtained from DoE approach. The selected three most significant variables were the initial concentration of Rhodamine B (30–70 mg/L), catalyst dosage (1.5–2.5 g/L) and ultrasonic power (40–80 W). Then, the concentrations of liquid sample were collected and measured using UV-vis spectrophotometer.

A range of C-N codoped TiO_2 NTs (molar ratios of N: Ti were 0.1, 0.3, 0.5 and 1.0) were synthesized using hydrothermal and calcination methods. These catalysts were characterized through SEM, TEM, EDX, elemental analysis (EA), XRD, FT-IR, nitrogen adsorption-desorption measurement, UV-vis DRS, TGA-DTA and X-ray photoelectron spectroscopy (XPS). The sonocatalytic activities of C-N codoped TiO_2 NTs were investigated under optimum conditions. This is followed by the characteristics and catalytic activities study of Fe-doped TiO_2 NTs with molar ratios of Fe to Ti were 0.001, 0.005, 0.01 and 0.02. The possible mechanism for sonocatalytic activation of Fe-doped TiO_2 NTs was proposed. Meanwhile, the generated intermediate products were detected through FT-IR analysis and gas chromatograph coupled with mass spectrometry (GC/MS).

On the other hand, characterization tests and evaluation of sonocatalytic activities on the reused TiO_2 NTs and Fe-doped TiO_2 NTs catalysts were also conducted. The characterization methods comprised of SEM, TEM, EDX, XRD, nitrogen adsorption-desorption isotherm, atomic absorption flame emission spectroscopy (AAS) and TGA for four catalytic cycles. The kinetic reaction and kinetic model for sonocatalytic degradation reaction of Rhodamine B was included. Then, the performance of sonocatalytic degradation of real textile wastewater was performed. All this information will be useful in promoting a better understanding of the optimum conditions for sonocatalytic degradation of organic dyes.

1.7 Organization of thesis

This thesis consists of five chapters. Chapter 1 gives brief introduction to water pollution especially in Malaysia, dye production, characteristics of textile industry effluent and its environmental impacts. Various types of wastewater treatment method with their advantages and disadvantages are discussed. Problem statements are then given after reviewing the scenario of current wastewater treatment methods. This section also highlights current problems faced by the textile industry and the importance of this research project. The objectives of this research project are then carefully divided with the aim of solving the problems faced by the textile industry. Finally, the organization of this thesis section highlights the contents of each chapter.

Chapter 2 gives an overall review of various research works reported in the literature in this research area. A review on the fundamentals of ultrasound, ultrasonic reaction system as well as sonolytic kinetic mechanism of water molecules is presented. The recent works on the sonocatalytic degradation of organic dyes by using TiO_2 are given. Next, a review on the synthesis methods for TiO_2 NTs, formation mechanism, post calcination and modifications of TiO_2 NTs is also presented. This is followed by the review of characterization techniques used to study the properties of the un-doped and doped TiO_2 NTs. Besides, the effects of various operating variables on the performance of the sonocatalytic degradation of organic dyes and the optimization study by means of DoE approach are reviewed. The mechanism of oxidation degradation of Rhodamine B is thoroughly reviewed and subsequently, followed by the catalyst reusability studies. The reaction kinetic and Langmuir-type model based on heterogeneous reaction systems for sonocatalytic degradation of organic dye are reviewed.

In Chapter 3, chemicals, materials and methodologies involved in this study are described in detail. It starts by listing all the chemicals and reagents used with their purity, followed by the overall flow of the research work and experimental setup. The preparation and characterizations of TiO_2 NPs and TiO_2 NTs, optimization studies using conventional one factor at a time and DoE approach are included. The following section describes the preparation, characterizations and sonocatalytic activities of C-N codoped and Fe-doped TiO_2 NTs. The details on the collection of liquid sample for determination of concentration and intermediate product analysis are given. Then, the catalyst reusability studies, reaction kinetic and

Langmuir-type model study are presented. This is followed by describing the performance of sonocatalytic degradation of real textile wastewater.

Chapter 4 is the most important chapter in the thesis. It encompasses the detail discussion on the results obtained in the present research work. The first section presents the characterizations of prepared TiO_2 NPs and annealed-TiO_2 NTs catalysts. This is followed by a study on the effect of parameters such as initial concentration of Rhodamine B, catalyst dosage, solution pH, ultrasonic frequency, ultrasonic power, H_2O_2 dosage, solution temperature and the use of dissolved air. DoE approach is used to optimize three significant variables that are, initial concentration of Rhodamine B, catalyst dosage and ultrasonic power. The next section reports on the preparation, characterizations and sonocatalytic activities of C-N codoped and Fe-doped TiO_2 NTs. The formation of intermediate products after sonocatalytic degradation of Rhodamine B is also studied. The reusability of catalyst is evaluated based on changes in the characteristics and catalytic activity in sonocatalytic degradation of Rhodamine B. Besides, reaction kinetics based on Langmuir-type model fitting for the sonocatalytic degradation is also presented. In the final section, adsorption followed by sonocatalytic degradation of real textile wastewater using Fe-doped TiO_2 NTs is investigated.

Chapter 5 gives a summary on the important findings made in this research work. Suggestions and recommendations to improve the present work as well as the future extension to the current study are also presented.

CHAPTER 2

LITERATURE REVIEW

2.1. Fundamentals of ultrasound

Ultrasound is defined as a sound wave with a frequency that is greater than the upper limit of human hearing ability, approximately 20 kHz and wavelength is about 75 mm (Khanal *et al.*, 2007; Thangavadivel *et al.*, 2009). The transmission of ultrasound waves that impose a sinusoidally varying pressure across an aqueous phase can cause the occurrence of cavitation as shown in Figure 2.1 (Leong *et al.*, 2011). Cavities (tiny micro bubbles) can be created during the expansion cycle with sufficient intensity with the distance between water molecules exceeding the critical molecular distance (10^{-8} m) (Vajnhandl and Majcen Le Marechal, 2005). During the expansion cycle, bubbles may grow rapidly and cause the dissolution of gases in the liquid to diffuse into the bubbles. Gasses that have diffused into the bubbles will be expelled into the fluid during the compression cycle.

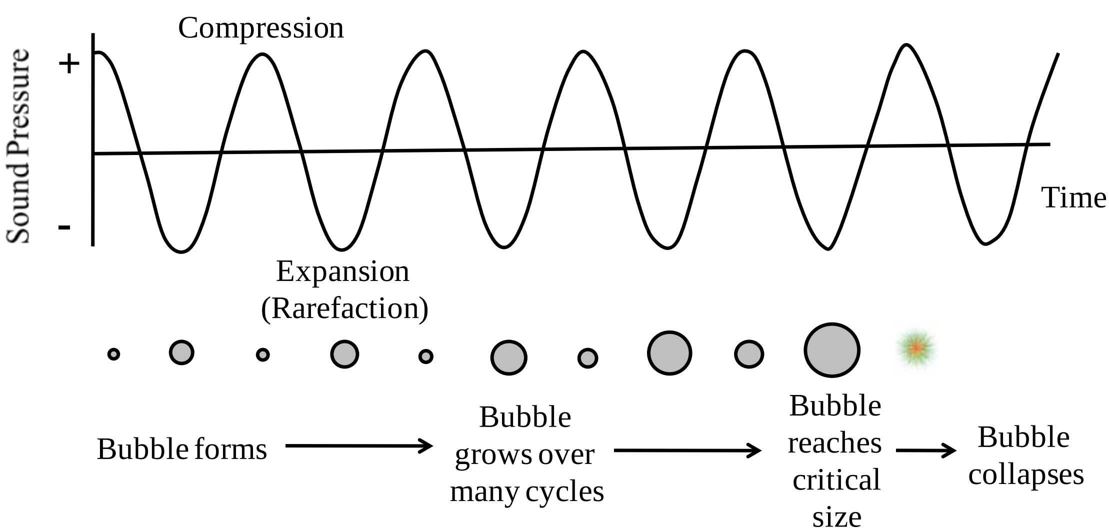


Figure 2.1: Graphical summary of the event of bubble formation, bubble growth and subsequent collapse over several acoustic cycles (Leong *et al.*, 2011).

Cavitation bubbles will grow over a few cycles by entrapping most of the vapour from the medium to reach a critical size before the implosion of the bubbles occurs as shown in Figure 2.2 (Suslick, 1989). The radius of the bubble before collapse when irradiated at 20 kHz is estimated to be in the order of several hundred micrometers. The time scale for the collapse of bubbles is less than 100 nanoseconds (Kotronarou *et al.*, 1992). The effective lifetime is less than 2 microseconds after which they start to collapse (Suslick, 1990). In summary, the phenomenon of cavitation consists of the repetitive and distinct three steps: formation (nucleation) and rapid growth (expansion) during the compression/ rarefaction cycles until they finally reach a critical size. After that, they start to undergo violent collapse (implosion) in the liquid (Ghodbane and Hamdaoui, 2009).

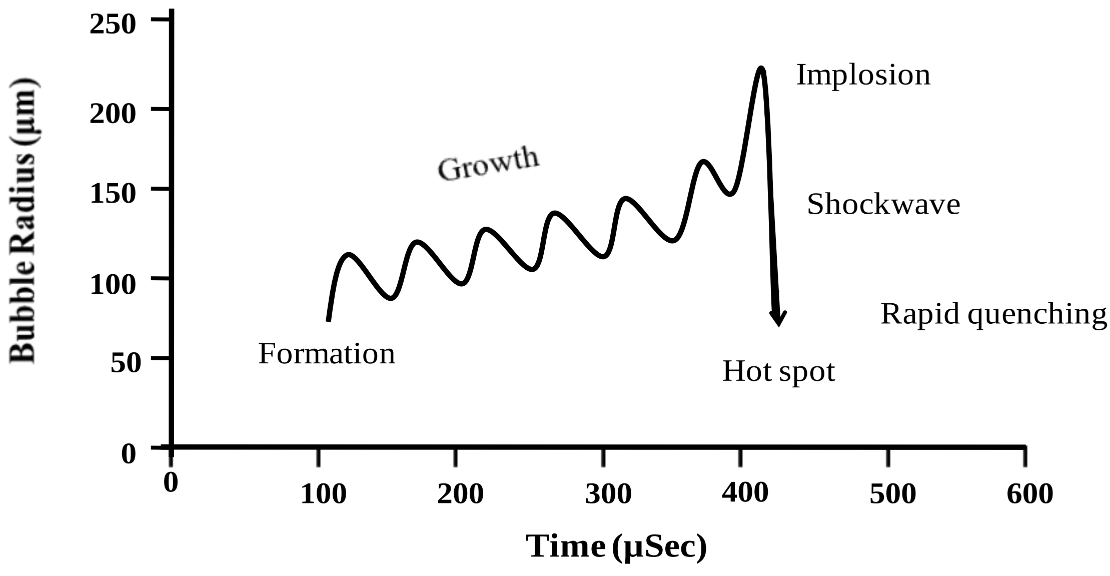


Figure 2.2: Formation, growth and implosion of cavitation bubble in aqueous solution with ultrasonic irradiation bubbles (Suslick, 1989).

2.1.1. Sonolytic kinetic mechanism of water molecules

The presence of dissolved oxygen (O_2) is reported to improve sonolysis reactions. However, it is not necessary for water (H_2O) sonolysis because sonolysis can proceed in the presence of any gas such as air, nitrogen, argon and hydrogen (Adewuyi, 2001). Ultrasound will induce the splitting of water molecules with the presence of dissolved oxygen and causes reactions (2.1)–(2.12) to occur (Adewuyi, 2001; Zhou *et al.*, 2013). In these reactions, ‘)))’ denotes the ultrasonic irradiation.

Thermal dissociation of H_2O and dissolved O_2 molecules in the cavities will convert them into reactive species such as •OH, hydrogen (•H), •O and hydroperoxyl radicals (•OOH) (reactions (1)–(5)). After that, the reactive radicals can enter into a variety of chemical reactions in the cavitation bubble and/or in the bulk solution. In the absence of any solutes, these primary radicals could recombine to form H_2O, •O and O_2 and then released into the bulk solution (reactions (2.6)–(2.8)).

H_2O_2 will be formed outside the hot bubbles or at the cooler interface as a consequence of •OH and •OOH recombination (reactions (2.9) and (2.10)). On the other hand, the •H and •OH species may further react with H_2O_2 as shown in reactions (2.11)–(2.12). The radicals (•OH and •OOH) may also reach the liquid-bubble interface and may pass into bulk solution where they can react with solutes.

$$H_2O \xrightarrow{)))} \bullet OH + \bullet H \quad (2.1)$$

$$O_2 \xrightarrow{)))} 2\bullet O \quad (2.2)$$

$$\bullet OH + \bullet O \rightarrow \bullet OOH \quad (2.3)$$

$$\bullet H + O_2 \rightarrow \bullet OOH \quad (2.4)$$

$$\bullet O + H_2O \rightarrow 2\bullet OH \quad (2.5)$$

$$\bullet OH + \bullet H \rightarrow H_2O \quad (2.6)$$

$$2\bullet OH \rightarrow H_2O + \bullet O \quad (2.7)$$

$$\bullet OOH + \bullet OH \rightarrow O_2 + H_2O \quad (2.8)$$

$$2\bullet OH \rightarrow H_2O_2 \quad (2.9)$$

$$2\bullet OOH \rightarrow H_2O_2 + O_2 \quad (2.10)$$

$$\bullet OH + H_2O_2 \rightarrow \bullet OOH + H_2O \quad (2.11)$$

$$\bullet H + H_2O_2 \rightarrow \bullet OH + H_2O \quad (2.12)$$

2.1.2. **Ultrasonic reaction systems**

There are three possible reaction zones in sonolysis liquid (Ghodbane and Hamdaoui, 2009; Moumeni and Hamdaoui, 2012) i.e. inside of the cavitation bubble, interfacial region between cavitation bubbles and bulk liquid and in the bulk solution. The temperatures of the interior and interfacial regions of the cavitation bubbles in alkanes as determined by Suslick *et al.* (1986) were 5200 K and 1900 K, respectively. Meanwhile, the temperature of the interfacial region of cavitation bubbles in the water supercritical phase was only 647 K (Hua *et al.*, 1995).

The reaction pathway depends on the volatility and hydrophobicity of the compound (Moumeni and Hamdaoui, 2012). Hydrophobic compounds with high volatility can be thermally decomposed inside the cavitation bubbles while hydrophilic with less or non-volatile organic compounds can be indirectly decomposed in the bulk liquid phase through the reaction with reactive radicals such as •OH (Son *et al.*, 2012). The highly reactive radicals could diffuse from the cavitation bubbles to the interfacial region and bulk solution when large temperature gradient exists (David, 2009).

On the other hand, nano-particles with sizes less than those of cavitation bubbles have higher cavitation erosion resistant and are easier to approach the interfacial region (bubbles surface) during the expansion cycles of ultrasound (Lampke *et al.*, 2008; Morel *et al.*, 2008). Figure 2.3 (a) shows the effective reaction zone (interfacial region) where very high concentration of •OH is achieved after the bubbles collapse (Morel *et al.*, 2008). The concentration that could be reached is estimated to be as high as 4 mM (Lu and Weavers, 2002).

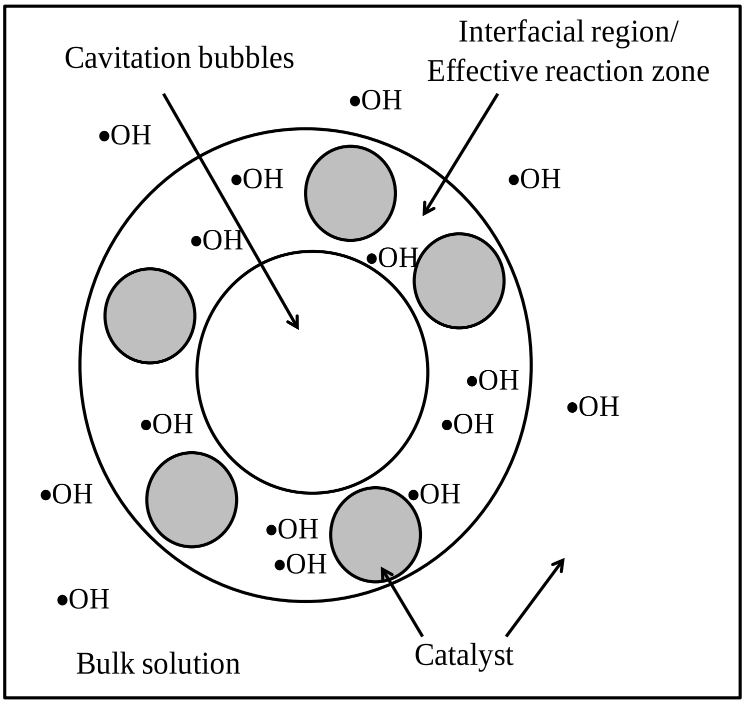


Figure 2.3: Schematic representations of effective reaction zone in cavitation bubbles (Morel *et al.*, 2008).

The asymmetric collapse of cavitation bubbles near the micro-particle surface will generate high-speed micro-jets of liquid in the order of 100 m/s (Suslick, 1990).

This may cause direct erosion (damage) on the particle's surface and de-aggregation of particles (Eren, 2012). Besides, the solid particles will experience a decrease in particle size and an increase in reactive surface area available for the subsequent reaction. The severity of the cavitation erosion that cause pitting and cracking of the particle surface is strongly influenced by the solid particle size (Chen *et al.*, 2007b).

2.2. Heterogeneous sonocatalytic degradation using titanium dioxide (TiO_2)

Many efforts have been devoted to improve the degradation efficiency in sonolysis processes. It is generally known that this process can be accelerated by the addition of various kinds of catalyst such as zinc oxide (ZnO) (Wang *et al.*, 2008a), iron oxide (Fe_2O_3) (Chen *et al.*, 2010) and copper oxide (CuO) (Zhang *et al.*, 2012). The presence of heterogeneous catalyst represents weak points in the liquid for nucleation of the cavitation bubbles to occur (Eren, 2012). The catalyst can enhance the dissociation of H_2O molecules (reaction 1) to increase the number of free radicals generated, thereby increasing the rate of degradation of the organic compound.

The most common type of catalyst to be used as sonocatalyst is TiO_2 due to its advantages such as inexpensive, non-toxic, chemically stable and long durability (Nakata and Fujishima, 2012). Table 2.1 summarizes reported findings on ultrasonic conditions, important conclusions and performance of TiO_2-based catalysts for enhancement of the degradation of recalcitrant organic compounds. It is generally reported that the optimum amount of catalyst is influenced by many factors such as initial dye concentration, irradiation intensity and type of catalyst (Gaya and Abdullah, 2008). Besides, it can be seen that there are optimum dopant/composite concentration of metals to achieve the highest degradation rate of organic pollutants.

Table 2.1: Sonocatalytic degradation of recalcitrant organic compounds by TiO_2-based catalysts.

No	Organic pollutants	Catalyst	Optimum reaction conditions	Important findings	References
1	Methyl Orange (MO)	(i) Rutile TiO_2 (ii) Transition crystal TiO_2	100 ml of 10 mg/l MO; 0.1 g of TiO_2; 40 kHz; 50 W[a]; 80 min	(i) The degradation rate of transition crystal TiO_2 (75 %) was higher than that of rutile TiO_2 (55.9 %); (ii) Inorganic anions: NO_2^-, NO_3^-, SO_4^{2-}	(Wang *et al.*, 2007b)
2	Basic Blue 41 (BB 41)	Nano-sized TiO_2	100 ml of 15 mg/l BB 41; 0.01 g of TiO_2; 35 kHz; 160 W[a]; 3 h	(i) H_2O_2 accelerated the degradation rate from 18 to 62 %; (ii) Apparent first-order reaction kinetics; (iii) Products: urea, nitrate, formic acid, acetic acid and oxalic acid	(Abbasi and Asl, 2008)
3	Phenol	Mixture of anatase and rutile TiO_2	7 l of 10 g/l phenol; 2 g/l of TiO_2; 25 kHz; 1 kW[a]; 206.3 kJ[b]; 3 h	(i) The degradation rate was increased from 12.2 to 37.8 % in the presence of UV irradiation, TiO_2 and H_2O_2. (ii) No intermediate products were reported.	(Khokhawala and Gogate, 2010)
4	2-chloro-5-methyl phenol (CMP)	Degussa P25 TiO_2	100 ml of CMP; 0.6-0.9 g of coal ash; 33 kHz; 1225 W[b]; 2 h	(i) The degradation rate was increased from 35 to 75 % in the presence of TiO_2 and H_2O_2; (ii) Apparent first-order reaction kinetics; (iii)The degradation rate was increased from 12 to 33 % in the presence of 100 mg/l of carbon tetrachloride (CCl_4) and decreased in the presence of 1 % of methanol.	(Nalini Vijaya Laxmi *et al.*, 2010)
5	Methyl parathion (MP)	Mixture of anatase and rutile TiO_2	100 ml of 20 ppm MP; 400 ppm of TiO_2; 20 kHz, 230 – 270 W[a]; 1 h	(i) The degradation rate was increased from 10.2 to 73.3 % in the presence of TiO_2, CCl_4, H_2O_2 and fenton reagent; (ii) Apparent first-order reaction kinetics	(Shriwas and Gogate, 2011)
6	Dinitrotoluene/ Trinitrotoluene	Nanometer rutile TiO_2	300 ml of 200 mg/l wastewater; 2 g/l of TiO_2; 20 kHz; 70 – 210 W[a]; 6 h	(i) The degradation rate was enhanced from 28 to 89 % in the presence of TiO_2 and oxygen dosage; (ii) Apparent first-order reaction kinetics; (iii) Products detected: toluene, mononitrotoluene, trinitrobenzene	(Chen and Huang, 2011)

Table 2.1 (Continued)

No	Organic pollutants	Catalyst	Optimum reaction conditions	Important findings	References
7	Methylene Blue (MB)	C-Cr codoped-TiO_2	100 ml of 10 mg/l MB; 0.1 g of catalyst; 40 kHz; 80 W[a]; 3 h	(i) Sonocatalytic degradation efficiency of C-Cr-TiO_2 (C: 1 wt. %, Cr: 1wt. %) was the highest (80 %), followed by undoped-TiO_2 (43 %), C-TiO_2 (20 %) and Cr-TiO_2 (22 %); (ii) No products and reaction kinetic were reported	(Zhang, 2012)
8	Azo Fuchsine (AF)	(i) Cr^{3+}-TiO_2 (ii) Co^{3+}-TiO_2	50 ml of 10 mg/l AF; 0.05 g of catalyst; 40 kHz; 50 W[a]; 2 h	(i) The degradation rate of 0.25 mol % Cr^{3+}-TiO_2 was 89 % followed by Co^{3+}-TiO_2 (45 %) and undoped TiO_2 (26 %); (ii) Apparent first-order reaction kinetics; (iii) Inorganic anions: NO_2^-, NO_3^-, SO_4^{2-}	(Wang *et al.*, 2009b)
9	Reactive Black 5 (RB5)	(i) TiO_2 (ii) CdS (iii) CdS/TiO_2	50 ml of 100 mg/l RB5; 0.05 g of catalyst; 20 kHz, 41 W[b]; 1 h	(i) The degradation rate of TiO_2/CdS (6:1) was the highest (94 %), followed by CdS (64 %) and TiO_2 (80 %); (ii) Inorganic anions: NO_3^-, SO_4^{2-}	(Ghows and Entezari, 2011)
10	Acid Red B (ARB)	(i) CeO_2/TiO_2 (ii) SnO_2/TiO_2 (iii) ZrO_2/TiO_2	50 ml of 10 mg/l ARB; 0.01 g of catalyst; 40 kHz; 50 W[a]; 100 min	(i) The degradation rate of CeO_2/TiO_2 (4:1) was 87 %, followed by SnO_2/TiO_2 (65 %) and ZrO_2/TiO_2 (40 %); (ii) Apparent first-order reaction kinetics	(Wang *et al.*, 2010b)
11	MO	$lnVO_4/TiO_2$	50 ml of $1x10^{-5}$ M solution; 0.03 g of catalyst; 28 kHz; 60 W[a]; 1 h	(i) $lnVO_4/TiO_2$ at 1:50 and 1:25 have highest sono- (80 %) and photo-catalytic activities (45 %), respectively; (ii) The degradation rate was increased in the presence of different oxidation reagents	(Min *et al.*, 2012)
12	ARB/ Methyl Violent/ Rhodamine B	(i) TiO_2 (ii) Al_2O_3/ TiO_2 (iii) Y_2O_3/ TiO_2 (iv) Fe_2O_3/ TiO_2	100 ml of 10 mg/l dyes solution; 40 kHz; 50W[a]; 100 min	(i) The degradation rate of Al_2O_3/ TiO_2 (4:1) was the 79 %, followed by Y_2O_3/TiO_2 (62 %), Fe_2O_3/TiO_2 (50 %) and TiO_2 (46 %); (ii) The degradation rate of ARB was 79 %, followed by Methyl Violent (60 %) and Rhodamine B (27 %)	(Chen *et al.*, 2011)

Note: [a]absolute power (where no data on specific acoustic power is given); [b]acoustic power determined by calorimeter method

Although the modification with transition metals is yet to be practical industrially, it provides a future for a successful and effective alternative in sonocatalytic degradation.

There has been no ready-made mechanism and satisfying explanation yet on the sonocatalytic degradation process in the presence of catalyst under ultrasonic irradiation. However, it is often reported that the possible mechanism should be based on both light and heat energies that come from the ultrasonic cavitation effect. The implosion of micro-bubbles will result in a short local sonoluminescence and hot spot conditions (localized generation of extreme conditions, high temperature and high pressure) (Guo *et al.*, 2011; Wang *et al.*, 2011c). The sonoluminescence can result in the formation of the light flash of average photon energy of 6 eV (Vinu and Madras, 2009). These light and energy are sufficient to excite the catalyst i.e. TiO_2 acting as a sonocatalyst, which causes some electrons to be transferred from the valence band to the conduction band. At the same time, the hole-electron pairs are formed. These holes and electrons will react with the absorbed H_2O molecules on the surface of TiO_2 particles and molecular O_2 dissolved in aqueous solution, respectively, to produce •OH and superoxides radical anion ($•O_2^-$). These highly reactive species are capable to attack various organic pollutants in wastewater.

2.3. TiO_2 nanotubes (NTs) catalyst

In terms of practical use, further development to improve the sonocatalytic activity of TiO_2 NPs is of great interest to current researchers. Three-dimensional (3D) TiO_2 NPs exhibits scattering effect of free electrons and electron trapping at the interface because of the formation of grain boundaries (Wang and Lin, 2010). It is well-known that grain boundaries often act as hole-electron recombination sites, thereby reducing electron mobility and exhibiting slow electron transport (Wang *et al.*, 2009c; Wang and Lin, 2010).

One-dimensional (1D) nanotubes have attracted extraordinary attention due to the unique physical and chemical properties. TiO_2 NTs are expected to facilitate electron transport due to the interconnections between nanotubes are greatly decreased in comparison with accumulated nanosized particles (Adachi *et al.*, 2004; Tan and Wu, 2006). Fast electron transport throughout the 1D channel may account for the excellent charge separation (Feng *et al.*, 2008). Mor *et al.* (2006) reported that the TiO_2 NTs array exhibited superior electron lifetimes than TiO_2 NPs. In addition to the effect on electron transport, TiO_2 NTs enhance the light scattering and harvesting due to the high length to diameter ratio (Wang *et al.*, 2009c). Besides, the special feature of TiO_2 NTs with its large surface area provided by inner and outer surfaces of the tubular structure is able to adsorb and reacts with more organic pollutant molecules. Thus, the use of highly crystalline anatase nanotubes is anticipated to be one of the most promising ways. To our knowledge, sonocatalytic degradation using TiO_2 NTs has yet to be reported.

Currently, the most common techniques to synthesize TiO_2 NTs comprised of template-assisted method, electrochemical anodization and hydrothermal method. Hoyer (1996) was the first researcher report to the preparation of TiO_2 NTs via a template-assisted method. Thereafter, the production of TiO_2 NTs materials was also reported by Kasuga *et al.* (1998) via hydrothermal method. Meanwhile, Gong *et al.* (2001) reported that uniform TiO_2 NTs arrays was obtained through anodic oxidation