FABRICATION, PHOTOCATALYTIC AND ADSORPTION OF IMMOBILIZED TiO$_2$/CHITOSAN-MONTMORILLONITE AND TiO$_2$/POLYANILINE BILAYER SYSTEMS FOR THE REMOVAL OF METHYL ORANGE DYE FROM AQUEOUS SOLUTIONS

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FABRICATION, PHOTOCATALYTIC AND ADSORPTION OF IMMOBILIZED TiO$_2$/CHITOSAN-MONTMORILLONITE AND TiO$_2$/POLYANILINE BILAYER SYSTEMS FOR THE REMOVAL OF METHYL ORANGE DYE FROM AQUEOUS SOLUTIONS

by

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IN THE NAME OF ALLAH THE MOST GRACIOUS AND MOST MERCIFUL

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Figure 4.3  Cross section of TiO$_2$/CS-MT/GP at different CS-MT loading; a) 2.24 mg cm$^{-2}$ (TiO$_2$) /1.27 mg cm$^{-2}$ (CS-MT), b) 2.24 mg cm$^{-2}$ (TiO$_2$) /1.92 mg cm$^{-2}$ (CS-MT) and c) 1.92 mg cm$^{-2}$ of CS-MT/GP

Figure 4.4  Pseudo first order rate constants of photocatalytic-adsorptive removal and adsorption by TiO$_2$/CS-MT/GP as a function of TiO$_2$ top layer loading at a fixed CS-MT sub-layer loading. (CS-MT loading = 1.27 mg cm$^{-2}$; [MO]$_o$ = 20 mg L$^{-1}$; pH = 6.5; aeration flow rate = 40 mL min$^{-1}$)

Figure 4.5  Cross section of TiO$_2$/CS-MT/GP at different TiO$_2$ loading; a) 1.27 mg cm$^{-2}$ (TiO$_2$) /1.27 mg cm$^{-2}$ (CS-MT), b) 2.54 mg cm$^{-2}$ (TiO$_2$) /1.27 mg cm$^{-2}$ (CS-MT) and c) 3.80 mg cm$^{-2}$ (TiO$_2$) /1.27 mg cm$^{-2}$ (CS-MT)

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Figure 4.16  TOC values during the photo-etching of TiO$_2$/CS-MT/GP and TiO$_2$/GP for 12 hours of treatment. (TiO$_2$ loading = 6.35 mg cm$^{-2}$; CS-MT loading = 3.18 mg cm$^{-2}$; pH = 6.5; aeration flow rate = 40 mL min$^{-1}$)

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Figure 4.23  Reusability of TiO$_2$/CS-MT/GP (photocatalytic-adsorptive removal), TiO$_2$/CS-MT/GP (adsorption) and TiO$_2$/GP (photocatalysis) for ten cycles based on pseudo first order rate constant. (TiO$_2$ loading = 2.54 mg cm$^{-2}$; CS-MT loading = 1.27 mg cm$^{-2}$; pH = 6.5; aeration flow rate = 40 mL min$^{-1}$)

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Figure 6.19  Pseudo first order rate constants of TiO$_2$/PANI/GP and TiO$_2$/GP before and after photo-etching. (TiO$_2$ loading = 1.27 mg cm$^{-2}$; PANI loading = 0.63 mg cm$^{-2}$; [MO]$_o$ = 20 mg L$^{-1}$; pH = 6.5; aeration flow rate = 40 mL min$^{-1}$)

Figure 6.20  TOC/TOC$_o$ values during the mineralization of TiO$_2$/PANI/GP and TiO$_2$/GP for 10 hours of irradiation. (TiO$_2$ loading = 3.18 mg cm$^{-2}$; PANI loading = 1.58 mg cm$^{-2}$; [MO]$_o$ = 20 mg L$^{-1}$; pH = 6.5; aeration flow rate = 40 mL min$^{-1}$)

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Figure 6.25  Ratio of pseudo first order rate constant of TiO$_2$/CS-MT/GP (photocatalytic-adsorptive removal) to TiO$_2$/CS-MT/GP (adsorption) and TiO$_2$/GP (photocatalysis). (TiO$_2$ loading = 1.27 mg cm$^{-2}$; PANI loading = 0.63 mg cm$^{-2}$; [MO]$_o$ = 20 mg L$^{-1}$; pH = 6.5; aeration flow rate = 40 mL min$^{-1}$).

Figure 6.26  The profile of LC-MS spectra of the identified MO and its intermediates after 1 hour of photocatalytic-adsorptive removal by the TiO$_2$/CS-MT/GP system using a) phosphate buffer: methanol and b) water: acetonitrile mobile phase

Figure 6.27  Proposed mechanism pathway during the photocatalytic-adsorptive removal of MO by TiO$_2$/PANI/GP.

Figure 7.1  Reusability of TiO$_2$/CS-MT/GP, TiO$_2$/PANI/GP and TiO$_2$/GP systems for ten cycles based on percentage of MO remaining. (TiO$_2$ (CS-MT) loading = 2.54 mg cm$^{-2}$; CS-MT loading = 1.27 mg cm$^{-2}$; TiO$_2$ (PANI) loading =1.27 mg cm$^{-2}$; PANI loading= 0.63 mg cm$^{-2}$; pH = 6.5; aeration flow rate = 40 mL min$^{-1}$)

Figure 7.2  Reusability of TiO$_2$/CS-MT/GP, TiO$_2$/PANI/GP and TiO$_2$/GP systems for ten cycles based on pseudo first order rate constant. (TiO$_2$ (CS-MT) loading = 2.54 mg cm$^{-2}$; CS-MT loading = 1.27 mg cm$^{-2}$; TiO$_2$ (PANI) loading = 1.27 mg cm$^{-2}$; PANI loading = 0.63 mg cm$^{-2}$; pH = 6.5; aeration flow rate = 40 mL min$^{-1}$)

Figure 7.3  Ratio of pseudo first order rate constant of photocatalytic-adsorptive removal to adsorption of TiO$_2$/CS-MT/GP and TiO$_2$/PANI/GP for ten cycles

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Figure 7.5 van’t Hoff’s plots for the adsorption of MO by TiO$_2$/CS-MT/GP and TiO$_2$/PANI/GP

Figure 7.6 PL spectra of (a) TiO$_2$/GP, (b) TiO$_2$/PANI/GP and c) TiO$_2$/CS-MT/GP

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Figure 7.8 The production of hydroxyl radicals (•OH) by a) TiO$_2$/CS-MT/GP, b) TiO$_2$/PANI/GP, c) TiO$_2$/GP and d) TA solution
### LIST OF ABBREVIATIONS

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<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>1,4-BQ</td>
<td>1,4-benzoquinone</td>
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<td>2,4-D</td>
<td>2,4-dichlorophenoxyacetic acid</td>
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<td>acid black 1</td>
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<td>APS</td>
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<td>BET</td>
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<td>brilliant green</td>
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<td>CS</td>
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<td>CS-MT/GP</td>
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<td>PANI/ENR&lt;sub&gt;50&lt;/sub&gt;/PVC</td>
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PEMFABRIKAN, FOTOMANGKINAN DAN PENJERAPAN SISTEM DWILAPISAN TERPEGUN TiO$_2$/KITOSAN-MONTMORILONIT DAN TiO$_2$/POLIANALINA UNTUK PENYINGKIRAN PEWARNA METIL JINGGA DARIPADA LARUTAN AKUEUS

ABSTRAK

Kajian ini adalah usaha untuk membangunkan dua sistem dwilapisan terpegun untuk penyingkirkan secara fotomangkinan-penjerapan pewarna metil oren (MO) daripada larutan akueus. Sistem dwilapisan terpegun melibatkan penjerap spesifik dan TiO$_2$ di atas plat kaca yang dinamakan TiO$_2$/kitosan-montmorilonit (TiO$_2$/CS-MT/GP) dan TiO$_2$/polianalina (TiO$_2$/PANI/GP) masing-masing telah difabrikasi melalui teknik pelitupan celup. Dalam kajian ini, CS-MT dan PANI berfungsi sebagai lapisan bawah manakala fotomangkin TiO$_2$ dijadikan sebagai lapisan atas. Pada awalnya, lapisan bawah untuk kedua-dua sistem dioptimumkan melalui kajian penjerapan dan dicirikan melalui mikroskop imbasan elektron (SEM), spektroskopi transformasi inframerah Fourier (FT-IR) dan analisis penjerapan-penyahjerapan N$_2$. Penambahan serbuk MT kepada matrik CS menurunkan kadar pembengkakan, menambahkan kekuatan mekanikal dan luas permukaan (S$_{BET}$) daripada 3.82 kepada 4.38 m$^2$ g$^{-1}$ manakala penambahan ENR$_{50}$-PVC menambahkan kekuatan mekanikal tetapi menurunkan S$_{BET}$ serbuk PANI daripada 9.16 kepada 8.50 m$^2$ g$^{-1}$. Penilaian aktiviti fotomangkinan oleh sistem dwilapisan dilakukan di bawah pancaran lampu pendarfluor kompak 45 Watt. Berat optimum lapisan penjerap adalah 1.27 dan 0.63 mg cm$^{-2}$ untuk masing-masing TiO$_2$/CS-MT/GP dan TiO$_2$/PANI/GP manakala berat TiO$_2$ optimum untuk TiO$_2$/CS-MT/GP dan TiO$_2$/PANI/GP masing-masing adalah 2.54 dan 1.27 mg cm$^{-2}$. Sistem TiO$_2$/CS-
MT/GP dan TiO₂/PANI/GP masing-masing mematuhi model kinetik penjerapan pseudo tertib pertama Lagergren dan pseudo tertib kedua Ho dan Mc Kay. Model isoterma Freundlich pula berupaya untuk menerangkan mekanisma penjerapan pada keseimbangan dan pembauran intra-zarah adalah salah satu kadar penghad untuk kedua-dua sistem. Sistem dwilapisan menghasilkan lebih radikal ·OH daripada sistem monolapisan TiO₂ kerana kadar pemisahan pasangan elektron-lubang yang lebih baik manakala jurang tenaga jalur TiO₂ dikurangkan dari 3.02 eV kepada 2.94 dan 2.95 eV, masing-masing untuk sistem TiO₂/CS-MT/GP dan TiO₂/PANI/GP. Keadaan operasi optimum bagi aktiviti fotomangkinan-penjerapan sistem dwilapisan adalah pH ambiien (6.5), kadar aliran udara 40 mL min⁻¹ dan kepekatan awal MO 20 mg L⁻¹. Sistem TiO₂/CS-MT/GP boleh mengekalkan kebolehulangan guna dalam purata penyingkiran sebanyak 97.7 ± 1.0 % dan kadar penyingkiran 0.088 ± 0.008 min⁻¹ sepanjang 10 kitaran manakala aktiviti fotomangkinan TiO₂/PANI/GP lebih baik pada tiga kitaran yang pertama tetapi menurun pada kitaran keempat dengan purata penyingkiran sebanyak 62.7 ± 10.2 % dan kadar penyingkiran adalah 0.017 ± 0.003 min⁻¹. Walau bagaimanapun, kadar penyingkiran sistem TiO₂/CS-MT/GP adalah 4 kali lebih baik dari TiO₂/GP manakala ia adalah 2.5 kali bagi sistem TiO₂/PANI/GP. Mineralisasi MO mencapai 82.8 % bagi TiO₂/CS-MT/GP dan 73.2 % bagi TiO₂/PANI/GP selepas 10 jam rawatan. Dalam pada itu, laluan penguraian menunjukkan spesis pertengahan utama yang terhasil adalah 4-{(E-[4-(metilamino)fenil]diazenil benzenasulfonat dan 4-{(E-[4-aminofenil]diazenil} benzenasulfonat. Secara perbandingan, sistem TiO₂/CS-MT/GP menunjukkan penyingkiran secara fotomangkinan-penjerapan pewarna MO yang lebih baik daripada sistem TiO₂/PANI/GP.
FABRICATION, PHOTOCATALYTIC AND ADSORPTION OF
IMMOBILIZED TiO$_2$/CHITOSAN-MONTMORILLONITE AND
TiO$_2$/POLYANILINE BILAYER SYSTEMS FOR THE REMOVAL OF
METHYL ORANGE DYE FROM AQUEOUS SOLUTIONS

ABSTRACT

This study was an effort to develop two immobilized bilayer systems for the photocatalytic-adsorptive removal of methyl orange (MO) dye from aqueous solution. The immobilized bilayer systems involving specific adsorbents and TiO$_2$ on the glass plates namely TiO$_2$/chitosan-montmorillonite (TiO$_2$/CS-MT/GP) and TiO$_2$/polyaniline (TiO$_2$/PANI/GP) systems had been fabricated via a dip coating technique. In this study, CS-MT and PANI, respectively functioned as the sub-layer while TiO$_2$ photocatalyst was made as the top layer. Initially, the respective adsorbent sub-layer of both systems was optimized via a batch adsorption study and characterized by using scanning electron microscopy (SEM), Fourier transform infra-red spectroscopy (FT-IR) and N$_2$ adsorption-desorption analysis. The addition of MT powder to CS matrix decreased the swelling degree, improved the mechanical strength and surface area (S$_{BET}$) of CS-MT from 3.82 to 4.38 m$^2$ g$^{-1}$ while the addition of ENR$_{50}$-PVC decreased the S$_{BET}$ of PANI powder from 9.16 to 8.50 m$^2$ g$^{-1}$ but improved its mechanical strength. The photocatalytic activity assessment of the bilayer systems was performed under the irradiation of a 45 Watts compact fluorescent lamp. The optimum adsorbent sub-layer loading was found to be 1.27 and 0.63 mg cm$^{-2}$ for TiO$_2$/CS-MT/GP and TiO$_2$/PANI/GP, respectively, while the optimum TiO$_2$ loading for TiO$_2$/CS-MT/GP and TiO$_2$/PANI/GP was 2.54 and 1.27 mg cm$^{-2}$, respectively. The TiO$_2$/CS-MT/GP and TiO$_2$/PANI/GP systems obeyed the
Lagergren’s pseudo first order and Ho and Mc Kay’s pseudo second order adsorption kinetic model, respectively. On the other hand, the Freundlich isotherm model could explain the adsorption mechanism at equilibrium whereas intra-particle diffusion was one of the rate limiting steps for both systems. The bilayer systems produced more 'OH radicals than the single layer TiO₂ due to better charge separation rate of electron-hole pairs while the band gap of TiO₂ was reduced from 3.02 eV to 2.94 and 2.95 eV for TiO₂/CS-MT/GP and TiO₂/PANI/GP system, respectively. The optimum operating conditions for the photocatalytic-adsorption activity of the bilayer systems were at ambient pH (6.5), 40 mL min⁻¹ of aeration flow rate and 20 mg L⁻¹ of MO initial concentration. The TiO₂/CS-MT/GP could maintain the reusability on the average removal of 97.7 ± 1.0 % and 0.088 ± 0.008 min⁻¹ removal rate throughout the 10 cycles, while the photocatalytic activity of TiO₂/PANI/GP was better at the first three cycles, but started to cease out at the 4th cycle with the removal average of 62.7 ± 10.2 % and 0.017 ± 0.003 min⁻¹ removal rate. Nevertheless, the removal rate of the MO of the TiO₂/CS-MT/GP system was 4 times better than TiO₂/GP while it was 2.5 times for the TiO₂/PANI/GP system. The mineralization of MO attained 82.8 % by TiO₂/CS-MT/GP and 73.2 % by TiO₂/PANI/GP after 10 hours of treatment. Meanwhile, the degradation pathways showed that the main intermediate species produced were 4-{(E-[4-(methylamino)phenyl] diazenyl}benzenesulfonate and 4-{(E-[4-aminophenyl] diazenyl}benzenesulfonate. Comparatively, the TiO₂/CS-MT/GP system showed better photocatalytic-adsorptive removal of the MO dye than the TiO₂/PANI/GP system.
CHAPTER ONE
INTRODUCTION

1.1 Photocatalysis: Historical Overview

Photocatalysis is defined as a photoreaction in the presence of a catalyst. This photoreaction is activated by photons from the light by appropriate energy (Mills and Le Hunte, 1997). According to Fujishima et al. (2008), the earlier work of photocatalysis had been reported by Renz at University of Lugano whereby he discovered that titania is partially reduced during the illumination of light in the presence of an organic compound, in which the oxide turns to dark colors (gray, blue and black) (Renz, 1921). Then, in 1924, Baur and Perret at the Swiss Federal Institute of Technology reported the photocatalytic deposition of metallic silver by ZnO. The studies were then continued for more years by different scientists and the progressed of those studies are shown in time frame as in Figure 1.1.

<table>
<thead>
<tr>
<th>Years</th>
<th>Research findings</th>
</tr>
</thead>
<tbody>
<tr>
<td>1921</td>
<td>Renz (1921) reported the partial reduction of titania under the light illumination in the presence of organic compound.</td>
</tr>
<tr>
<td>1927</td>
<td>Baur and Neuweiler (1927) discovered the photocatalytic deposition of a silver salt of metallic silver by ZnO and proposed Baur redox mechanism 1927.</td>
</tr>
<tr>
<td>1938</td>
<td>Goodeve and Kitchener (1938) proposed titania acted as the catalyst to accelerate the photochemical oxidation, studied other semiconductors and speculated on the precise mechanism.</td>
</tr>
</tbody>
</table>
1949: Jacobsen (1949) at the National Lead Company (USA) attempted to explain the paint chalking in terms of a redox mechanism.

1953: Markham and Laidler (1953) studied the photocatalytic reaction of ZnO as the photoanode for formation of H$_2$O$_2$ but neglected TiO$_2$ due to production of unmeasurable amount of H$_2$O$_2$.

1955: Stephens et al. (1955) at Wayne State University studied the production of H$_2$O$_2$ on several semiconductors and found that CdS is a more active photocatalyst than ZnO.

1958: Kennedy et al. (1958) at the University of Edinburgh found a correlation between the ability of TiO$_2$ sample to photocatalytically decompose chlorazol sky blue.

1964: Filimonov (1964) compared the photocatalytic oxidation of isopropanol to acetone on ZnO and TiO$_2$. They concluded that the mechanism of on TiO$_2$ involved reduction of O$_2$ to H$_2$O, while the O$_2$ reduction on ZnO was only to H$_2$O$_2$.

1965: McLintock and Ritchie (1965) studied the photocatalytic oxidation of ethylene and propylene at TiO$_2$ and proposed that it was possible to oxidize the organic compounds completely to H$_2$O and CO$_2$ which involved the production of superoxide from oxygen.

1967: Morrison and Freund (1967) found quantitatively that the availability of electrons and holes at the surface is dominant in the mechanism of a heterogeneously catalyzed reaction.

Figure 1.1: Time frame of photocatalysis research progress (Fujishima et al., 2008).
The historical breakthrough of photocatalysis was catalyzed by the demand of energy renewal and storage and the detoxification of harmful substances in water and air especially in the late 1960s (Ibhadon and Fitzpatrick, 2013; Linsebigler et al., 1995). In 1972, Akira Fujishima and his doctoral advisor, Kenichi Honda discovered the splitting of water by TiO$_2$ electrode in an electrochemical cell after an exposure to light of 415 nm wavelength (Fujishima and Honda, 1972). In the experiment (Figure 1.2), the photocurrent flowed from Pt counter electrode through the external circuit to TiO$_2$ electrode which was proven to cause the oxidation of water at the TiO$_2$ electrode with the evolution of oxygen while it was the reduction of water at the Pt electrode with the evolution of hydrogen (Nakata et al., 2012). Since then, there has been a growing interest in this discovery (oxidation and reduction potential of TiO$_2$) for numerous applications such as water splitting, hydrogen production, electrode and water/air treatment especially in the field of heterogeneous photocatalysis.

Figure 1.2: Schematic diagram of electrochemical photocell. (1) n-type TiO$_2$ electrode; (2) platinum black counter electrode; (3) ionically conducting separator; (4) gas buret; (5) load resistance; and (6) voltmeter (Hashimoto et al., 2005).
1.2 Heterogeneous photocatalysis

Application of photocatalysis is generally divided into homogeneous and heterogeneous photocatalysis. The homogeneous photocatalysis generally refers to the reactants and the photocatalysts existing in the same phase while the heterogeneous photocatalysis refers to photoreaction of a catalyst which is in a different phase from the reactants. Common examples of homogeneous photocatalysis are ozonation and photo-Fenton systems (Fe$^{2+}$ and Fe$^{2+}$/H$_2$O$_2$) (Kitsiou et al., 2009). Heterogeneous photocatalysis includes the process involving light irradiation on semiconductors namely TiO$_2$, ZnO, ZnS and CdS. Examples of heterogeneous photocatalysis are mild/total oxidation, dehydrogenation, hydrogen transfer, deuterium-alkane isotopic exchange, metal deposition, water detoxification and gaseous pollutant removal (Herrmann, 1999). The basic components of heterogeneous photocatalysis are (Teh and Mohamed, 2011):

1) An emitted photon of appropriate wavelength,
2) a strong oxidizing agent (O$_2$) and 
3) a catalyst surface of a semiconductor material.

A semiconductor can be a material with electrical resistivity between that of an insulator and a conductor while a semiconductor photocatalyst is characterized by an electronic band structure in which the highest occupied energy band, valence band (VB) and conduction band (CB) are separated by a band gap ($E_{bg}$). The CB is the energy level for the reduction potential of photoelectrons; VB is for the oxidizing ability of photogenerated holes while the band gap defines the wavelength sensitivity of the semiconductor to irradiation. The magnitude of the fixed energy gap between the electron rich valence band and the largely vacant conduction band governs the extent of the thermal population of the conduction band (Fox and Dulay, 1993). In
other words, the higher band gap of a semiconductor corresponds to shorter light wavelength which eventually requires a higher energy for electron excitation from the VB to CB. However, the electronic band of a semiconductor is often confused with the electronic band of a dye molecule. The difference between the energy level in a semiconductor photocatalyst and a dye molecule is shown in Figure 1.3.

![Diagram](image)

**Figure 1.3**: The energy level diagram of a) a semiconductor and b) a dye molecule.

According to Pankaj *et al*. (2013), a semiconductor must be non-toxic, stable in aqueous solution containing toxic or reactive chemicals and resistant to photocorrosion under sunlight. Numerous semiconductors have been tested for heterogeneous photocatalysis especially for the purpose of environmental remediation such as ZnO, ZnS and CdS. Unfortunately, these semiconductors suffer from photocorrosion in which the former photocatalyst (ZnO and ZnS) releases Zn(OH)$_2$ and Zn$^{2+}$ while the latter (CdS) releases Cd$^{2+}$ ions upon irradiation in aqueous media (Pankaj *et al.*, 2013). Titanium dioxide (TiO$_2$) on the other hand, possesses several important characteristics such as stable, non-toxic, and inert and is now considered an effective photocatalyst (Mills *et al.*, 2015).
1.3  Titanium dioxide

1.3.1  Ideal photocatalyst

The successful application of TiO$_2$ in water purification was firstly reported in 1977 (Frank and Bard, 1977) on cyanide and sulfite. The specialty of TiO$_2$ which made it differs from other photocatalyst is in mixings of both of its anatase and rutile forms (Li et al., 2006). With the attractive and successful degradation of many organic pollutants, TiO$_2$ has become the most chosen photocatalyst in the field of photocatalysis. Table 1.1 lists the characteristics of TiO$_2$ which closely matches the ideal photocatalyst characteristics.

Table 1.1: The characteristics match of ideal and TiO$_2$ photocatalyst (Hondow et al., 2010; Ibhadon and Fitzpatrick, 2013).

<table>
<thead>
<tr>
<th>Ideal photocatalyst</th>
<th>TiO$_2$</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photoactive</td>
<td>✓</td>
<td>High photoactivity in the presence of light.</td>
</tr>
<tr>
<td>Able to absorb visible and/or near UV light</td>
<td></td>
<td>Only active for light irradiation of wavelength $\lambda \leq 387$ nm however, it can be modified to adsorb light of $\lambda \geq 387$ nm.</td>
</tr>
<tr>
<td>Biologically and chemically inert</td>
<td>✓</td>
<td>Does not take part in the reaction whereby only acting as the mediator for redox reactions.</td>
</tr>
<tr>
<td>Photostable (not liable to photoanonic corrosion)</td>
<td>✓</td>
<td>Practical for long term use and applications</td>
</tr>
<tr>
<td>Inexpensive</td>
<td>✓</td>
<td>Naturally abundant resource of titanium</td>
</tr>
<tr>
<td>Non-toxic</td>
<td>✓</td>
<td>Safe for human and environment</td>
</tr>
<tr>
<td>Able to oxidize and reduce water to O$_2$ and H$_2$, respectively</td>
<td>✓</td>
<td>The photogenerated electron-holes can react with water via redox reaction to produce O$_2$ and H$_2$ since the band is larger than 1.23 eV.</td>
</tr>
</tbody>
</table>
1.3.2 Structure and properties

TiO$_2$ is a metal oxide with a molar mass of 79.90 g mol$^{-1}$ and classified as not hazardous by the United Nations (UN) Globally Harmonized System (GHS) of Classification and Labeling of Chemicals (IARC, 2010). The photocatalytic activity of TiO$_2$ is highly dependent on the geometry, crystalline phases, surface defects, specific surface area and particle sizes (Dai et al., 2015). There are three types of TiO$_2$ phase that are mostly studied; rutile, anatase and brookite as shown in Figure 1.4. Rutile is the most stable phase of TiO$_2$, followed by anatase and brookite which are metastable and can be transformed to rutile when heated (Kaplan et al., 2015). Other type of TiO$_2$ polymorphs namely TiO$_2$(B) and the layered titanates are rarely studied. However, the anatase has been reported to exhibit the best photoactivity among the three phases due to its efficiency in light harvesting, prolong the lifetimes of charge carriers and charge separation (Kaplan et al., 2015; Leyva et al., 2015). On the other hand, rutile phase suffers the weaker adsorption of organic pollutants and faster recombination of electron-hole pairs while brookite is difficult to synthesize (Zhang et al., 2011). In recent years, the preparation of mixed phase TiO$_2$ is actively being studied such as anatase-rutile (Wu et al., 2015; Zhang et al., 2015b; Zhang et al., 2015), anatase-TiO$_2$(B) (Dai et al., 2015; Parayil et al., 2013), and anatase-brookite (Zhang et al., 2011).

The commercial mixed phase TiO$_2$ (anatase and rutile) is currently available in the market, namely Millenium 1580 S, Kronos 7500 and Kronos 1002 and Evonik P-25 or Aeroxide P25 (Montes et al., 2014). Aeroxide P-25 TiO$_2$, which was used in this study, consists of 80 % of anatase and 20 % of rutile. According to the product information from Evonik, P-25 TiO$_2$ has a surface area of 50 ± 15 m$^2$ g$^{-1}$ and average particle size of 21 nm. The mixture of anatase and rutile in P-25 TiO$_2$, enhances the
photoactivity due to low recombination of electron-hole pairs as a result of relative conduction band edge between the anatase and rutile (Dai et al., 2015). P-25 TiO$_2$ has become the standard photocatalyst among the other brand of TiO$_2$ as it exhibits good photoactivity for the degradation of varieties of pollutants whereby it became the main reason of the selection for this study.

Figure 1.4: The crystal structures of TiO$_2$: (a) anatase, (b) rutile and (c) brookite (Leandro et al., 2013).

1.3.3 Mechanism of the TiO$_2$ photocatalysis

The process of photocatalysis is initiated when light of appropriate wavelength was absorbed by TiO$_2$ photocatalyst. According to physic’s law, the wavelength is inversely proportional to the band gap energy. Therefore, the light wavelength should be similar or less than 380 nm since the band gap energy should be similar or greater than the band gap of TiO$_2$ for electron excitation from the valence to the conduction band to occur. The reaction on TiO$_2$ is shown as follows (Singh et al., 2013; Zangeneh et al., 2015):
Figure 1.5: Schematic energy diagram of TiO$_2$ as adapted from Kazuhito et al. (2005).

Step 1: Generation of photoholes and electrons:

\[ \text{TiO}_2 + \text{hv} \rightarrow \text{TiO}_2 (e^-_{\text{CB}}) + \text{TiO}_2 (h^+_{\text{VB}}) \quad (1.1) \]

Step 2: Formation of hydroxyl radicals (\(^{\cdot}\text{OH}\)) by the photogenerated holes at valence band:

\[ \text{H}_2\text{O} + h^+_{\text{VB}} \rightarrow \text{H}^+ + \text{^{\cdot}\text{OH}} \quad (1.2) \]
\[ \text{OH}^- + h^+_{\text{VB}} \rightarrow \text{^{\cdot}\text{OH}} \quad (1.3) \]

Step 3: Formation of superoxide anion radical (O$_2^{-}$), hydroperoxyl radical (\(^{\cdot}\text{OOH}\)), hydrogen peroxide (H$_2$O$_2$) and hydroxyl radicals at the conduction band:

\[ \text{O}_2 + e^-_{\text{CB}} \rightarrow \text{O}_2^{-}\cdot \quad (1.4) \]
\[ \text{O}_2^{-}\cdot + \text{H}^+ \rightarrow \text{^{\cdot}\text{OOH}} \quad (1.5) \]
\[ \text{^{\cdot}\text{OOH}} + \text{^{\cdot}\text{OOH}} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad (1.6) \]
\[ \text{H}_2\text{O}_2 + e^-_{\text{CB}} \rightarrow \text{OH}^- + \text{^{\cdot}\text{OH}} \quad (1.7) \]
\[ \text{H}_2\text{O}_2 + \text{O}_2^- \rightarrow \cdot\text{OH} + \cdot\text{OH} + \text{O}_2 \quad (1.8) \]

Step 4: Oxidation of organic contaminant (R):

\[ \text{R} + \cdot\text{OH} \rightarrow \rightarrow \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (1.9) \]

\[ \text{R} + \text{O}_2^- \rightarrow \rightarrow \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (1.10) \]

\[ \text{R} + h^+_{\text{VB}} \rightarrow \text{R}^{\cdot} \rightarrow \text{the degradation products} \quad (1.11) \]

\[ \text{R} + e^-_{\text{CB}} \rightarrow \text{R}^- \rightarrow \text{the degradation products} \quad (1.12) \]

A successful photocatalytic oxidation of organic pollutants by TiO\textsubscript{2} is highly dependent on the production of \cdot\text{OH radicals at the VB of TiO\textsubscript{2}. However, the generated \cdot\text{OH radical is unstable and must be continuously generated in situ, by chemical or photochemical process (Leandro et al., 2013). Unless there are electron acceptors at the CB of TiO\textsubscript{2} after the excitation, the excited electrons could recombine with the photogenerated holes at the VB. Moreover, the recombination of electron-hole pairs would produce heat, which is unfavorable for the efficacy of the photocatalyst activity.}

### 1.3.4 Langmuir-Hinshelwood kinetic model

The Langmuir Hinshelwood equation was commonly used as to describe the heterogeneous photocatalysis. The equation of the Langmuir Hinshelwood kinetic model is given as in Equation 1.13 (Kumar et al., 2008a).

\[ r = -\frac{dC}{dt} = \frac{k_\text{r}KC}{1 + KC'} \quad (1.13) \]

where \( r \) is the rate of reaction that changes with time.
The term $r$ in Equation 1.13 was represented in terms of initial reaction rate, $r_o$, as a function of the initial dye concentration, $C_o$, or in terms of $C_e$, where $C_e$ is the equilibrium dye concentration in solution. The initial rate of reaction as a function of $C_o$ and $C_e$ is given by Equations 1.14 and 1.15, respectively:

$$r_o = \frac{k_r C_o}{1 + K C_o}$$  \hspace{1cm} (1.14) \\
$$r_o = \frac{k_r C_e}{1 + K C_e}$$  \hspace{1cm} (1.15)

The parameter $k_r$ and $K$ which is a function of $C_o$ or $C_e$ can be predicted by linearizing Equations 1.14 and 1.15 as follows:

$$\frac{1}{r_o} = \frac{1}{k_r} + \frac{1}{k_r K C_o}$$  \hspace{1cm} (1.16)

The constants $k_r$ and $K$ can be calculated from the corresponding integrated expression between the limits: $C = C_o$ at $t = 0$ and $C = C_t$ at $t = t$. The integrated expression is given by:

$$\ln \left( \frac{C_o}{C_t} \right) + K (C_o - C) = k_r K t$$  \hspace{1cm} (1.17)

If the term $KC << 1$, the equation (1.13) is reduced to:

$$r = \frac{dC}{dt} = k_r K C$$  \hspace{1cm} (1.18)

Integrating equation (1.18) with respect to limits: $C = C_o$ at $t = 0$ and $C = C_t$ at $t = t$, the Langmuir Hinshelwood expression reduces to a pseudo first order kinetic and is given by:

$$\ln \left( \frac{C_o}{C_t} \right) = k_f K t = k t$$  \hspace{1cm} (1.19)

where the new constant $k$ includes $k_r$ and $K$. 

11
A plot of $\ln\left(\frac{C_0}{C_t}\right)$ versus time ($t$) will give a straight line with the slope of $k$ as the pseudo first order rate constant. The coefficient of determination ($R^2$) indicates the degree of agreement of the reaction with the Langmuir-Hinshelwood kinetic model, where:

- $r$: the rate of degradation ($\text{mg L}^{-1} \text{ min}$);
- $C_e$: the equilibrium concentration of pollutant ($\text{mg L}^{-1}$);
- $C_o$: the initial concentration of pollutant ($\text{mg L}^{-1}$);
- $C_t$: the concentration of pollutant at time $t$ during degradation ($\text{mg L}^{-1}$);
- $K$: equilibrium constant for adsorption of the substrate onto catalyst;
- $k_r$: limiting rate constant of reaction at maximum coverage under the given experimental conditions;
- $r_o$: initial rate of reaction ($\text{min}^{-1}$);
- $t$: the irradiation time (min);
- $k$: the reaction rate constant ($\text{min}^{-1}$).

### 1.3.5 Drawbacks and improvements

Though many researchers had reported the excellent performance by TiO$_2$ photocatalyst in water abatement, it suffers from several drawbacks such as high recombination rate of electron-hole pairs and poor degradation rate for some organic pollutants. Therefore, the research progress in photocatalysis field continues to grow and new methods are being developed in order to overcome those obstacles.

The first intrinsic problem with TiO$_2$ photocatalyst was its high recombination rate of electron-hole pairs upon light irradiation. It was known that the lifetime of charge carriers in TiO$_2$ after excitation was very short which is 10-40 $\mu$s.
(Colbeau et al., 2003). The short lifetime due to high recombination of charge carriers could be overcome by surface sensitization using dye or metal complexes in order to induce better charge separation. The dye is anchored on TiO$_2$ surface by covalent, or physical or chemical bonding which induced the charge injection of the excited dye molecule into the CB of TiO$_2$ leading to successive photocatalytic degradation. This sensitization also increases the range of wavelength response towards the natural sunlight (Gupta and Tripathi, 2011). However, the dyes themselves can be photodegraded to form intermediates which need to be disposed. On the other hand, transition metal complexes such as Ru-polypyrindyl complexes induce the charge separation by the excited electrons which participate in the charge transfer of electrons to TiO$_2$ conduction band (Kalyanasundaram and Grätzel, 1998).

The second drawback of TiO$_2$ is the excitation of electron-hole pairs could be only initiated in the presence of high UV light intensity. Therefore, the solution is to change the band gap energy by coupling two semiconductors of suitable potential energy such as CdS-TiO$_2$, SnO$_2$-TiO$_2$ and ZnO-TiO$_2$ whereby the holes produced in smaller band gap semiconductor remain while the electrons are transferred to the conduction band of TiO$_2$ which induce charge separation (Jing and Guo, 2006). Another way is to dope TiO$_2$ with noble metals such as Ag (Albiter et al., 2015; Gomathi and Mohan, 2010), Au (Subramanian et al., 2003; Tahir et al., 2006; Zhu et al., 2009), Pt, Ni, Rh and Cu (Gupta and Tripathi, 2011) which can trap the electrons and free holes and enhance the charge separation at the valence band to participate in the photocatalytic oxidation reaction. This was due to the Fermi levels of these noble metals which are lower than that of TiO$_2$. Nevertheless, it was found that the properties of these TiO$_2$-noble metal composites are strongly dependent on the size of metal particle, composition and dispersion as if the concentration of metal was too
high, the absorption of the light photon would be reduced and the metal can become the electron-hole recombination centers which resulted in lower efficiency than the TiO$_2$. TiO$_2$ can also be doped with non-metal such as C,N,B,F (Valentin and Pacchioni, 2013) and carbon nano tube (CNT) (Ashkarran et al., 2015). The composites could decrease the band gap which make it visible light active. In addition, the TiO$_2$ could be also modified by co-doping the metal-metal such as Fe$^{3+}$ and Eu$^{3+}$ (Vasiliu et al., 2009), metal-non-metal; Cu-N (Song et al., 2008) and non-metal-non-metal; C-N (Nawawi and Nawi, 2014; Sabri et al., 2015). The TiO$_2$ co-doped system showed a red-shift in absorption spectrum and high photocatalytic activity than the single doped TiO$_2$ especially when exposed to total visible light.

Thirdly, the conventional TiO$_2$ in suspended or slurry mode requires post treatment due to its nanoparticle size, which is a tedious, time and money consuming filtration process. Apart from filtration, the steps of recovering the photocatalyst from the treated water solution involved the process of washing, filtering and drying, which may result in the lost of an amount of the photocatalyst during the process. To solve this drawback, different supports and immobilization techniques were used whereby the common support materials and their immobilization modes were glass beads; heat attachment (Daneshvar et al., 2005), granular activated carbon; dip hydrothermal (Wang et al., 2009), stainless steel; coating (Souzanchi et al., 2013) and glass plate; dip coating (Razak et al., 2014). However, the immobilization mode of TiO$_2$ might have some significant defects such as reducing the active sites exposure to light, as the area is fixed and the mass transfer hindrance increases, which lead to poor photocatalytic activity plus the need to seek for well-defined procedures and equipment (Singh et al., 2013). Coupling the photocatalyst and adsorbent in the immobilized form is another approach to enhance the overall
photocatalytic performance. TiO\(_2\) has been combined with various adsorbents such as silica oxide (SiO\(_2\)) (Rahman et al., 2014), montmorillonite (MT) (Bhattacharyya et al., 2004), activated carbon (AC) (Muthirulan et al., 2013) and chitosan (CS) nanofiber (Razzaz et al., 2016) whereby all systems showed enhanced photocatalytic performance than the bare TiO\(_2\) in the removal of the organic contaminants.

1.4 Chitosan (CS)

1.4.1 Origin of CS

Chitin is firstly identified in 1884 and is originated from the main component on shell of crustaceans such as shrimp and crab shell and cell walls of fungi and yeast (Younes and Rinaudo, 2015). Chitin was the second most abundant polysaccharides in nature after cellulose while CS is the derivation of chitin which had undergone the deacetylation process using NaOH as the deacetylation agent (Choi et al., 2016). Figure 1.6 provides the chemical structures of cellulose, chitin and CS. Chitin with more than 75 \% degree of deacetylation is known as CS while cellulose only differs with chitin and CS based on the hydroxyl group in its C-2 position. The process of deacetylation removes acetyl groups from the molecular chain of chitin and leaving behind a complete amino group (-NH\(_2\)). The degree of deacetylation depends on the content of the amino groups in the CS. Increasing temperature and strength of NaOH enhances the acetyl group removal from chitin, which then produces CS with different properties. CS was one of the main cationic polymers which forms inter and intra-molecular hydrogen bonding due to amine and hydroxyl groups which made the crystalline structure of CS rigid (Choi et al., 2016).
1.4.2 Applications of CS

CS is biodegradable, biocompatible, bioadhesive, hydrophilic, able to produce film and a good adsorbent (Zhao et al., 2015). The diverse properties of CS made it usable in different applications and fields such as pharmaceutical, biomedical, food, cosmetics (Rinaudo, 2006) and waste water remediation (Cárdenas et al., 2002; Janaki et al., 2012; Ngah and Fatinathan, 2010). The functionality of CS was based on the presence of hydroxyl and amino group which served as the coordination and reaction sites for modification which could attract the positive and negative chemical species to bound to its structure (Ngah and Fatinathan, 2010).

CS can also become bioadhesive since it offers a very good strength as compared to synthetic adhesive without containing volatile organic carbon (VOC)
(Patel, 2015). However, the material suffers from low strength and large shrinkage upon dehydration. Therefore, other materials such as clay when added into the CS matrix can significantly improve its thermal stability and mechanical properties, and may exert special behavior towards chemical species present in water (Wang et al., 2006). Such a system can also be used to fasten flocculation and improve the flake's textures (Shou et al., 2012).

### 1.4.3 Modification of CS

CS is not soluble in organic solvents and only dissolved in acidic aqueous media (HCl and CH$_3$COOH) whereby the solubility of CS is facilitated by the protonation of its primary amino group on the C-2 position of the D-glucosamine. The degree of protonation depends on the pKa of the acid and CS concentration which only converts CS into the pseudonatural cationic polymer (García et al., 2015; Rinaudo et al., 1999). Due to its excellent and vast properties, CS was modified chemically in order to produce novel CS-based materials or biohybrid with specific application properties which usually occurs at the –NH$_2$ primary group and hydroxyl group at the C-2 and C-6 position, respectively (García et al., 2015). However, due to its poor solubility in organic solvents, researchers have focused on improving its solubility and grafting process by attaching new functional groups. Garcia et al. (2015) had reported a novel and simple method via nitrooxide-mediated polymerization (NMP) to modify well-defined molecular weight CS in homogeneous media by utilizing CS-sodium dodecylbenzenesulfonate (SDBS)-glycidyl methacrylate (GMA) as a precursor. The poly (styrene) (PS), poly (butyl acrylate) (PBA), poly (acrylic acid) (PAA) respectively, are grafted onto the hydroxyl groups of CS-SDBS-GMA in DMSO to produce CS-GMA-PS, CS-GMA-PBA and CS-GMA-PAA as new CS based materials. Cai et al. (2009) prepared the soluble CS in
DMSO by grafting organo-soluble polymers, poly (ethyleneglycol) (PEG) and poly (\(\varepsilon\)-caprolactone) (PCL) onto CS using the acidic CS and sodium dodecylsulfate (SDS) solution as an intermediate. The authors found that the PEG and PCL became conjugated to CS through the hydroxyl groups while maintaining the cationic density of the amino groups intact on the surface of the CS. The SDS and SDBS which were responsible for the dissolution of grafted CS in DMSO could be removed by precipitation of the grafted polymer in DMSO into Tris aqueous solution or dialyzing against Tris solution (Cai et al., 2009; García et al., 2015).

Meanwhile, the CS films, beads, gels and fibers which were prepared by single CS solution suffer dehydration shrinkage in aqueous media and swelling defects upon thermal treatment. In addition, the solubility of CS in acidic media can be cumbersome, which eventually decrease the spectrum of its application (Ngah et al., 2005). To overcome this, the CS was modified chemically by cross-linkers such as epichlorohydrin (ECH), glutaraldehyde (GLA), glyoxal, ethylene glycol diglycidyl ether (EDGE), tripolyphosphate (TPP) and genipin (Berger et al., 2004; Obeid et al., 2013) basically to change the hydrophilicity of CS to be more hydrophobic. The cross-linking occurs in the amine and hydroxyl groups in C-2 and C-6 position that allows the formation of bridges between the polymer chains. Among the cross-linking agents, the dialdehydes such as GLA and glyoxal bind preferentially to the amino group of CS forming covalent imine bonds via a Schiff reaction while the epoxides, such as ECH prefers to bind to the free hydroxyl group (Berger et al., 2004). The cross-linked CS has an improved mechanical resistance, strength and stability in acidic, alkaline and chemical solution as well as under thermal treatment and compression (Azlan et al., 2009; Ngah et al., 2002). However, cross-linking agents such as GLA is known to be neurotoxic while glyoxal is
mutagenic, which may not be a good choice for biomedical, medical, pharmaceutical and tissue engineering applications (Berger et al., 2004).

Recently, the attention has been devoted to modifying the CS structure by combining with other potential materials such as zeolite and MT. The hydrophilic CS forms composite with clays which are alumino-silicates with a three-dimensional framework structure containing AlO$_4$ and SiO$_4$. Such combination would avoid the use of toxic and mutagenic chemicals which can harm human health. In addition, the combination of the two different types of adsorbents could improve the pore size, mechanical strength, chemical stability, hydrophilicity and biocompatibility of CS (Ngah et al., 2012). Another approach in modification of CS was via photo irradiation which causes changes in the polymeric structure of CS by inducing the chain scission, reducing the average molecular weight, improving solubility in water, changing the color intensity, optical and spectral sensitivity (Taei, 2011). CS has been modified by different light sources such as UV light (Praxedes et al., 2012), fluorescent lamp (Jawad and Nawi, 2012b), ultrasonic irradiation (Cravotto et al., 2005; Kasaai et al., 2008) and gamma ($\gamma$) rays (Kang et al., 2007; Tahtat et al., 2012). Nevertheless, until recently, the oxidative degradation are based on the formation of reactive $`$OH radicals from H$_2$O$_2$ (Chang et al., 2001), TiO$_2$ (Jawad and Nawi, 2012b) and O$_3$ (Yue et al., 2009) which are powerful oxidizing species. It receives attention whereby modification occurs when the oxidative radical species attack the 1,4 glycosidic linkages which result in the CS degradation (Kang et al., 2007). Modification of CS by a combination of photon from light source and oxidants could turn CS into the desired properties such as water-soluble, low molecular weight with added specialty in biological, chemical and physical properties than that of the ordinary CS (Kang et al., 2007).
1.5 Montmorillonite

1.5.1 Structure and properties

Montmorillonite (MT), the clay mineral is often confused with bentonite. Both bentonite and MT belong to the smectite group which is built from 2:1 aluminosilicate whereby alumina octahedral is switched between two tetrahedral of silica layers (Bhattacharyya and Gupta, 2008). In short, bentonite can be considered as the family name while MT is the species name. MT is referred to as “swelling clay minerals” due to the tendency for polar liquids to be taken in the interlayer space which makes MT a matrix for the preparation of functional composites in adsorbents, catalyst and flame retardants (Sun et al., 2015).

![Figure 1.7: The structure of MT. Source: http://sparc.fpv.umb.sk/ (accessed on 9.10 pm, 21st Feb 2016).](image)

The clay layer is characterized by permanent negative charges due to isomorphous substitution of Al$^{3+}$ atoms of the octahedra for lower valent cations (Mg$^{2+}$). Exchangeable cations (Na$^+$) are present in the interlayer spaces to
compensate the negative charge. In addition to the permanent charge, pH-dependent charge is present on the edges of clay layer; Al–OH (or Si–OH) groups at the edges are present as different states depending on the pH of the solution: Al–OH\(^{2+}\) (at low pH), Al–OH (at medium pH), and Al–O– (at high pH). Other than MT, there are several kinds of smectite-type clay minerals (e.g., saponite, hectorite, beidelite, and nontronite), which differ in chemical composition and the type of isomorphous substitution. Most of these clay minerals occur naturally in earth soils, whereas the composition, isomorphous substitution, impurity level, and crystallinity of the clays differ depending on the production areas. Synthetic clay minerals, which are suitable for chemical experiments due to lower impurity content, are also available (Nakato and Miyamoto, 2009).

1.5.2 Applications of MT in environmental remediation

The interlayer of MT contains negative charges which are counterbalanced by inorganic cations (e.g., Na\(^+\), Ca\(^{2+}\)) and exchangeable for adsorption of cationic contaminants such as heavy metals, cationic dyes (methylene blue (MB), malachite green (MG)) and cationic surfactants (Zhu et al., 2014). Since MT adsorbs cationic surfactant, it can undergo ion-exchange with its negative charge counterpart which the modified MT often called organo-MT was produced. Eventually, the modification can promote the adsorption of anionic contaminants such as humic acid, methyl orange (MO), 2-naphthol and neutral pollutant such as phenol (Jiang et al., 2002). Beside organic pollutants, organo-clays can also adsorb heavy metals such as Cu\(^{2+}\) and Zn\(^{2+}\) (Lin, 2002), Cr (VI) (Krishna et al., 2000) and Ni\(^{2+}\) (Ijagbemi et al., 2009). The properties of clays specifically MT as good adsorbents are due to their high specific surface area, high chemical and mechanical stability, cheap and vastly available from nature. Thus, MT has the potential to be widely used in wastewater
treatment for removing many types of pollutants and heavy metals besides activated carbon, a universal but costly adsorbent which restricts its wide application (Zhu et al., 2014).

1.6 Conducting polymer: Polyaniline

The breakthrough discovery of intrinsically conducting polymer (ICP) was initiated by MacDiarmid, Heeger and Shirakawa in 1977 whereby they discovered the exposure of polyacetylene to iodine vapor yielding conducting material (MacDiarmid, 2001). ICPs are completely different form the conducting polymers which are merely a physical mixture of conducting material (eg; metal or carbon powder) and a nonconductive polymer. ICPs on the other hand, are commonly known as a “synthetic metal” which possess the electrical, electronic, magnetic and optical properties of a metal while retaining the mechanical properties and processability (MacDiarmid, 2001). Recently, ICPs discovered were polypyrrole (Ppy), polythiophene, polyparaphenylene (PPP) and polyparaphenylene vinylene (PPV) (Bhadra et al., 2009).

Polyaniline (PANI), known as “aniline black” was rediscovered in 1980s (Čirić, 2013). PANI emerged as the promising material in the family of conducting polymers which allow the construction of polymer modified electrodes to be used as sensors, biosensors, and substrates for metallization (Ahmed, 2004). PANI has controlled conductivity within $10^{-10} - 10^1$ S cm$^{-1}$ range with ionic and proton conductivity, redox activity, electro- and solvatochromism, electrical storage, stable in extreme condition, high thermal stability and easy to synthesize (Ahmed, 2004; Yu and Shishov, 2012). The synthesis of PANI has expanded over the years and it became the most studied conducting polymer. Under different conditions, PANI can
exist in three main oxidation states as shown in Figure 1.8. The oxidation states on the other hand, are denoted by the $y$ values as shown in Figure 1.9 whereby $y = 1$, 0.5 and 0 corresponding to the fully reduced polyaniline (benzenoid diamine), the half oxidized polyaniline (emeraldine), and the fully oxidized polyaniline (quinoid diimine), respectively (Wang et al., 2013b). According to Bhadra et al. (2009), the mode of synthesis was varied which were based on chemical, electrochemical, template, enzymatic, plasma and photo approaches. The most common method, chemical approach can be subdivided into the following modes as shown in Table 1.2.

![Figure 1.8: Structures of polyaniline in various intrinsic redox states (Chen, 2007)](image)

![Figure 1.9: Molecular structure of emeraldine base of PANI (Zeng and Ko, 1998).](image)
Table 1.2: Various methods for synthesis of PANI (Bhadra et al., 2009).

<table>
<thead>
<tr>
<th>Method</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>Heterophase</td>
<td>Polymerization includes the precipitation, suspension, micro suspension, emulsion, miniemulsion, microemulsion, dispersion, reverse micelle and inverse (Carenza and Palma, 1985)</td>
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<tr>
<td>Solution</td>
<td>Processability is better since the prepared PANI is already in a solution (Kuramoto and Tomita, 1997).</td>
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<tr>
<td>Interfacial</td>
<td>Polymerization is carried out in a mixture of two immiscible solvents such as water and chloroform in the presence of different acids as dopants (Chen et al., 2007; Dallas et al., 2007).</td>
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<tr>
<td>Seeding</td>
<td>A typical template approach whereby foreign material is used as a seed. PANI obtained is similar to a nanofiber with high conductivity which dependent on the type and concentration of acids, the type of seed, solvent and the relative amount of seed to solvent (Xing et al., 2006).</td>
</tr>
<tr>
<td>Metathesis</td>
<td>PANI is formed when ( p )-dichlorobenzene and sodium amide is heated at 220 °C for 12 hours in an organic medium such as benzene, whereby aniline monomer is not required (Guo et al., 2005).</td>
</tr>
<tr>
<td>Self assembling</td>
<td>The PANI films are grown on the film by polymerizing an aniline monomer in a vapor phase (Yang et al., 2007)</td>
</tr>
<tr>
<td>Electrochemical</td>
<td>i) Constant current (galvanostatic) Two-electrode assembly dipped in an electrolyte solution containing monomer, with specified current (Genies et al., 1985)</td>
</tr>
<tr>
<td></td>
<td>ii) A constant potential (potentiostatic) PANI powder adheres weakly on the electrode (Diaz and Logan, 1980).</td>
</tr>
<tr>
<td></td>
<td>iii) A potential scanning/cycling or sweeping (Diaz and Logan, 1980).</td>
</tr>
<tr>
<td>Sonochemical</td>
<td>Dropwise addition of an acidic ammonium persulfate (APS) solution to an acidic aniline solution with the aid of ultrasonic irradiation. The possible reactions within the system are (Jing et al., 2007):</td>
</tr>
<tr>
<td></td>
<td>i) the continuous formation of primary PANI nanofibers;</td>
</tr>
<tr>
<td></td>
<td>ii) the conversion of primary nanofibers into thicker fibers with uneven surfaces; and</td>
</tr>
<tr>
<td></td>
<td>iii) the growth and agglomeration of thicker.</td>
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