IMMOBILIZED TiO_2/ACTIVATED CARBON BILAYER SYSTEM FOR THE REMOVAL OF PHENOL VIA PHOTOCATALYTIC-ADSORPTIVE PROCESSES

NOOR NAZIHAH BINTI BAHRUDIN

UNIVERSITI SAINS MALAYSIA

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by

NOOR NAZIHAH BINTI BAHRUDIN

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IN THE NAME OF ALLAH THE MOST GRACIOUS AND MOST MERCIFUL

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TABLE OF CONTENTS

LIST OF TABLE

LIST OF FIGURES

LIST OF PLATES

LIST OF ABBREVIATIONS

AC	Activated carbon
$AC/ENR_{50}/PVC$	Activated carbon/ epoxidized natural rubber/polyvinyl chloride single layer system
BET	Brunauer-Emmet-Teller
CHN	Carbon, Hydrogen, Nitrogen
COD	Chemical oxygen demand
e^-	Negatively charged electron
EDX	Energy dispersive X-ray
ENR_{50}	Epoxidized natural rubber of 50 % mole epoxidation
FTIR	Fourier transform infra red
h^+	Positively charged hole
O_3	Ozone
pH_{pzc}	pH at point of zero charge
PL	Photoluminescence
PVC	Poly (vinyl) chloride
SEM	Scanning electron micrograph
TGA	Thermogravimetric analysis
TiO_2	Titanium dioxide
$TiO_2/AC/ENR_{50}/PVC$	Titanium dioxide/ activated carbon/epoxidized natural rubber/polyvinyl chloride bilayer system
$TiO_2/ENR_{50}/PVC$	Titanium dioxide/epoxidized natural rubber/polyvinyl chloride single layer system
UV	Ultraviolet
W	Watt

SISTEM DWILAPISAN TiO_2/KARBON TERAKTIF TERIMMOBIL UNTUK PENYINGKIRAN FENOL MELALUI PROSES FOTOPEMANGKINAN-PENJERAPAN

ABSTRAK

Titanium dioksida (TiO_2) dan karbon teraktif (AC) telah digabungkan dalam satu sistem pemegunan susunan dwilapisan di atas plat kaca untuk penyingkiran fenol. Sistem monolapisan AC/ENR_{50}/PVC dan dwilapisan TiO_2/AC/ENR_{50}/PVC terpegun telah berjaya dibangunkan melalui kaedah penyaduran celup mudah. Pelekat yang digunakan dalam larutan penyaduran celup mudah AC/ENR_{50}/PVC dan TiO_2/ENR_{50}/PVC ialah campuran ENR_{50}/PVC. Tujuan pemegunan ialah untuk menyingkirkan fenol daripada larutan akues secara fotopemangkinan dan dibandingkan dengan kaedah lama iaitu kaedah ampaian. Kajian kinetik dan isoterma penjerapan ke atas AC/ENR_{50}/PVC dan TiO_2/AC/ENR_{50}/PVC juga telah dijalankan yang mana kedua-dua sistem mengikut model kinetik aturan kedua Lagergren tetapi untuk kajian isoterma, sistem AC/ENR_{50}/PVC mengikut Langmuir manakala sistem TiO_2/AC/ENR_{50}/PVC mengikut isoterma Freundlich. Berat optimum AC/ENR_{50}/PVC adalah 2.54 mg cm^{-2} manakala berat TiO_2/ENR_{50}/PVC di atas lapisan AC/ENR_{50}/PVC dalam sistem dwilapisan TiO_2/AC/ENR_{50}/PVC adalah 0.32 mg cm^{-2}. Didapati bahawa sistem dwilapisan TiO_2/AC/ENR_{50}/PVC berfungsi melalui gabungan dua proses secara serentak iaitu penjerapan fenol ke dalam lapisan AC/ENR_{50}/PVC dan fotopemangkinan fenol oleh lapisan TiO_2/ENR_{50}/PVC. Lapisan TiO_2/ENR_{50}/PVC mengikut pemalar kadar aturan pseudo pertama Langmuir Hinshelwood manakala lapisan AC/ENR_{50}/PVC menunjukkan kadar aturan pseudo kedua. Oleh yang demikian, TiO_2/AC/ENR_{50}/PVC mengikut pemalar kadar aturan kedua kerana proses penjerapan lebih baik daripada proses

fotopemamngkinan di dalam sistem dwilapisan. Kesan-kesan parameter seperti pH larutan, keamatan cahaya dan bekalan O_2 juga dikaji dan didapati optimum masing-masing pada pH larutan 6, 6 W m^{-2} kebocoran UV dan 100 mL min^{-1} kadar pengudaraan. Perbandingan di antara TiO_2/AC/ENR_{50}/PVC dan TiO_2/ENR_{50}/PVC adalah berdasarkan keefisienan penyingkiran fenol untuk semua parameter yang dikaji. Kadar mineralisasi fenol dikaji melalui ujian Keperluan Oksigen Kimia. Kebolehgunaan dan ujian Keperluan Oksigen Kimia juga telah dijalankan di bawah iradiasi cahaya matahari untuk aplikasi asas. SEM-EDX, BET, FT-IR, CHN, PL dan TGA adalah merupakan beberapa pencirian fizikal digunakan untuk menerangkan fenomena sebelum dan selepas aplikasi.

IMMOBILIZED TiO_2/ACTIVATED CARBON BILAYER SYSTEM FOR THE REMOVAL OF PHENOL VIA PHOTOCATALYTIC-ADSORPTIVE PROCESSES

ABSTRACT

Titanium dioxide (TiO_2) and activated carbon (AC) had been combined in an immobilized bilayer arrangement on glass plates for the removal of phenol. The immobilized monolayer AC/ENR_{50}/PVC and bilayer TiO_2/AC/ENR_{50}/PVC systems have been successfully fabricated via a dip-coating method. The adhesives used in both activated carbon and TiO_2 dip-coating solutions were ENR_{50}/PVC blends. The purpose of the fabrication was to photocatalytically remove phenol from aqueous solution as opposed to the conventional suspension method. Adsorption kinetic and isotherm studies of TiO_2/AC/ENR_{50}/PVC and AC/ENR_{50}/PVC were also conducted whereby both systems followed second order kinetic model of Lagergren's but for isotherm study, the TiO_2/AC/ENR_{50}/PVC system obeyed Langmuir whereas the AC/ENR_{50}/PVC system obeyed Freundlich. The optimum AC/ENR_{50}/PVC loading was 2.5 mg cm^{-2} while the optimum TiO_2/ENR_{50}/PVC loading on the AC/ENR_{50}/PVC layer was 0.32 mg cm^{-2}. It was found that the TiO_2/AC/ENR_{50}/PVC bilayer system operated simultaneously via the incorporation of the two processes i.e adsorption of phenol into the AC/ENR_{50}/PVC layer and photocatalytic degradation of phenol by the TiO_2/ENR_{50}/PVC layer. The single layer of TiO_2/ENR_{50}/PVC followed pseudo first order rate constant of Langmuir-Hinshelwood equation whereas the single layer of AC/ENR_{50}/PVC showed the pseudo second order rate constant. Therefore, TiO_2/AC/ENR_{50}/PVC followed the pseudo second order rate constant since the adsorption process was more favourable than the photocatalytic process in the bilayer system. The effects of some operational parameters such as pH of

the solution, light intensity and O_2 supply were also studied and were found to be optimized at pH 6, 6.0 Wm^{-2} of UV leakage and 100 mL min^{-1} of aeration rate, respectively. The comparison between TiO_2/AC/ENR_{50}/PVC and TiO_2/ENR_{50}/PVC was based on the removal efficiency for all the parameters studied. The mineralization of phenol was observed through COD test. The reusability and COD tests were also done under solar irradiation for practical applications. SEM-EDX, BET, FT-IR, CHN, PL and TGA are some physical characterizations used to describe the process phenomenon before and after applications.

CHAPTER 1: INTRODUCTION AND LITERATURE REVIEWS

1.1 Water Pollution: Law Enforcement, Treatment and Remediation Technology

About 70% of earth surface is surrounded by water. This abundance source of water is essential for the sustenance and continuation of all living things. The generation of electricity, crops plantation, and others are water-dependence in nature that carry economical values for a nation as well as the whole world. The increasing human population means increasing activities that somehow generate waste discharges that pollute the water sources. The discovery of new findings results in a growth of many kinds of industries such as pharmaceuticals, textiles, plastics, cosmetics and etc. The industrial wastes usually contained numerous types of chemical as well as biological species like algae, pathogens and viruses of fatal diseases that contribute towards acute toxicity in the contaminated water.

For decades, researchers and scientists have been continuously searching for the best method to treat the effluents and wastes before they are released to the mainstreams. The government and private sectors made an effort in funding researches in universities in order to gain the best method for wastewater remediation. Apart from that, many acts and enforcements had been established in order to protect the environment from an environmental disorder. As in Malaysia, the Environmental Quality Act 1974, Act 127 Section 29 [1] stated that,

(1) No person shall, unless licensed, discharge environmentally hazardous substances, pollutants or wastes into the Malaysian waters in contravention of the acceptable conditions specified under section 21.*[Am. Act 636:s.12]*.

(2) Any person who contravenes subsection (1) shall be guilty of an offence and shall be liable to a fine not exceeding five hundred thousand ringgit or to imprisonment for not exceeding five years or to both.*[Am. Act A953:s.15]*

The current technologies in wastewater remediation had pursued a great innovative development than the earlier pioneers of the technology. The flocculation, activated sludge, and carbon adsorption, are some examples of existing and conventional techniques that are now vastly considered as not that effective in terms of poor treatment of pollutant, cannot be re-used, costly, as well as generating secondary pollutants. A new concept of green technology reveals the need of decomposition and mineralization of pollutants into harmless compound as the final products such as CO_2, H_2O and NH_4^+, NO_3^- and other mineral species. The ideal and green chemistry is said to be having the following characteristics as indicated in Table 1.1 [2-3]:

Table 1.1: Characteristics of ideal and green chemistry

Cost effective	Design for energy efficiency
Use of renewable feedstock	Prevention
Reduce derivatives	Mineralize toxic species
Catalysis	Atom economy
Design for degradation	Safer solvents and auxiliaries
Stable	Designing safer chemicals
Real-time analysis for pollution prevention	Safer chemistry for accident prevention

In general, there are three types of treatment to remove pollutants from the wastewater; physical, biological and chemical. Table 1.2 shows some of the applications of the three modes of water treatment technologies. However, the drawbacks that led to a decrement in the removal efficiency and reusability of each treatment technique tend to diminish the ‘dream’ of ideal and green wastewater

Table 1.2: Available technologies for use in the wastewater treatment

Treatment modes	Processes	Operation
Biological	Microbial degradation	Degradation using microbial xenobiotic metabolism [4]
	Adsorption by microbial biomass	Accumulation of organics/inorganics in microorganism [5]
	Bioremediation	Microorganisms to mitigate/ eliminate hazardous pollutants [6]
	Enzymatic treatment	Phase transfer or partial polymerization of tyrosinase, laccase and horseradish peroxidase enzymes [7]
Physical	Nanofiltration	Membrane pretreatment using microfiltration and ultrafiltration [8]
	Reverse osmosis	Pressure-driven processes occur by solution-diffusion mechanism [9]
	Electrodialysis	Membrane-based separation process to separate ionic species using electrically charged membrane and electrical potential difference [10]
	Adsorption	Adsorption is a separating process in which the adsorbates are attracted to the interior and exterior surfaces of adsorbent [11]
Chemical	Coagulation/Flocculation	Use of coagulants and flocculants in solid-liquid separation processes [12]
	Electroflotation	Float pollutants by their adhesion onto tiny bubbles of H_2 and O_2 from electrolysis of aqueous. [13]
	Electronic coagulation	Generates metallic OH flocs in situ via electro-dissolution of a soluble anode [14]
	Oxidation (ozone)	Ozone (O_3) acts as oxidant for organic pollutants to low molecular weight substances [15]
	Irradiation	Exposure of pollutants to the source of radiant energy [16]
	Advanced Oxidation Process (AOP)	Pollutant oxidation occurs via highly reactive intermediate, the hydroxyl radical($HO^{\cdot}$) [17]

treatment technology. Biological treatment for example suffers from the sewage that are non-biodegradable, production of inert matter as well as toxic metabolites from the microbial metabolism of contaminants [18].

1.2 Phenol

The discovery of phenol (hyroxybenzene) at the end of eighteen century made a history to scientists at that moment. Firstly isolated in crude form, pure phenol was then isolated in 1834 and the structure was proven in 1842. Classical uses of phenol included as wound dressing and antiseptic in surgery. Phenol exists as a white solid in pure form, possesses a sweet but irritating smell and can dissolve well in water and organic solvent despite of moving slower than water in the air. The products originated from phenol normally easy to catch fire and get burnt [19].

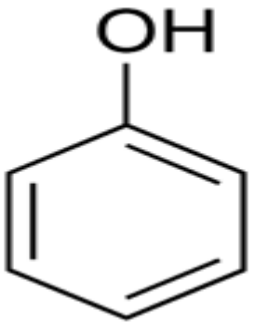

Figure 1.1: Molecular structure of phenol

For industrial scale, phenol was largely synthesized (<95%) from the extraction of coal tar formed by the transformation of high quantities of cumene present in plants that were used for the tar production. Apart from that, other

chemical reactions that produce phenol are alkylation of benzene with propene, chlorobenzene and sodium hydroxide as well as toluene-benzoic acid oxidation process. In nature, phenol is formed from various sources such as chemical reactions in condensed water vapour that forms clouds at atmosphere, biosynthesis by plants, decomposition of organic matter, tyrosine transformation in mammalian digestive tract and from amino acids contained in plants' hemicelluloses under the influence of sun rays [20].

At present, phenol is utilized to make plastics, nylon 6 and other man-made fibers as well as bisphenol A for the production of epoxy and other resins. Large amount of phenol is generated from oil refineries, coal gasification, petrochemical units, as well as leachates emerging from waste disposal produced by microbial hydrolysis and the photodegradation of organophosphorous pesticides [21]. In addition, the manufacturing industries and wasteland filling release many phenol-based chemicals into the atmosphere, groundwater, surface water bodies as well as soils and rocks [7]. With so many listed sources producing phenol, it is undeniable that our water sources are in harm of phenol contamination. It is also no doubt that phenol was one of the first compounds inscribed in The List of Priority Pollutants by the US Environmental Protection Agency (EPA) with the maximum amount of 1 mg L^{-1} permitted in water bodies [22].

Phenol possesses carcinogenic, teratogenic and mutagenic properties as well as causes histopathological changes and acute toxicity for man's health. The toxicity of phenol stems from unspecified toxicity related with hydrophobicity of the individual compound, formation of free radicals and localization of the meta-para substituent. For example, phenolic compounds can mimic the oestradiol hormones that influence the development and maintenance of female characteristics while

bisphenol A may function as endocrine disrupting chemical. The active transformation of phenol after penetration of the cell membrane may form electrophilic metabolites that can bind and damage DNA or enzymes [20, 23].

The structure of phenol and its properties made it the parent of multi compounds that are produced in the industries such as chlorophenol, catechol, nitrophenol, bisphenols, aminophenols and methylphenols. Since phenol is a stable compound, the breakdown of its compound onto linear chain compound seems a big challenge. In addition, when phenol-containing water is chlorinated, the removal of toxic chlorinated phenolic compounds from the wastewater source to a safety level (0.1-1.0 mg L^{-1}) is not an easy task [23]. Moving on to the world of environmental green policy, it is an urge to find the ideal wastewater treatment that would solve the problem of removing this toxic and anthropogenic compound. Owing to this, advanced oxidation process (AOPs) can be a suitable candidate.

1.3 Environmental Photocatalysis

Advanced Oxidation Processes (AOPs) got its name from the chemical oxidation based process via hydroxyl radicals. A few methods that were based on AOPs are ozonation (O_3, O_3/UV, O_3/H_2O_2 and O_3/UV/H_2O_2), UV processes (UV and UV/H_2O_2), photocatalytic process (TiO_2/UV, semiconductor/UV) and Fenton process (H_2O_2/Fe^{2+}, H_2O_2/Fe^{3+}) [17]. Among those mentioned processes, photocatalysis is nearly closed to being the ideal and the most prominent treatment method in meeting clean energy demand and solving environmental pollution. A total number of 10,624 publications until the year 2010 (Source: ISI Web of Knowledge, 13/05/2011, search terms: “photocatalysis”) had been recorded which proved that there was a dramatic

rise of interest in photocatalysis. Its wide attractive applications are namely: water splitting of hydrogen generation, self-cleaning activity, air purification, degradation of pollutants in wastewater as well as carbon dioxide remediation [24].

In the environmental photocatalysis for wastewater treatment, molecules such as pesticides (herbicides, insecticides, fungicides, etc.) or dyes are totally destroyed and mineralized into CO_2 and innocuous inorganic anions (Cl^-, SO_4^{2-}, NO_3^-) [25]. Beside the selective mild oxidation of organic pollutants, many toxic inorganic ions can also be oxidized to their upper oxidation state which is harmless. For example, SO_3^{2-} is oxidized to SO_4^{2-} whereas CN^- to OCN^- and subsequently to NO_3^- and CO_3^{2-}. Heavy metal cations such as Pd^+, Hg^+, Ag^+ can be deposited as crystallites on TiO_2 surface after reduction by photoelectrons. Noble metal such as photographic Ag could be removed and separated from common metals baths [3]. In addition, this hydroxyl radicals-based reaction is the most viable method that can remove pollutants to a level as low as ppb (part per billion) [26].

Photocatalysis mediated semiconductor can operate under visible and UV region. In UV region, UV light with different wavelengths that range from UVC (200-290 nm), UVB (290-320 nm) and UVA (320-400 nm) can be used for the photocatalytic irradiation sources. For clinical issue, UVB can excite the DNA's molecules whereas UVA can generate reactive oxygen species in nucleic acids, proteins and lipids. UVC rays, on the other hand, have less clinical interest since they do not reach earth's surface. UV rays can cause skin damage such as erythema, immuno suppression, skin cancers and photo aging via the interaction between molecular components with epidermis and dermis [27]. However, in photocatalysis, ultraviolet (UV) irradiation source stands up among other sources due to the high energy band gap of some semiconductors. Since sunlight is an abundantly natural

energy source for UV irradiance, its energy can be conveniently exploited for the irradiation of semiconductor. In this case, the photocatalytic material must have high activity in regards to the process of interest with high efficiency of solar energy conversion. Semiconductor such as ZnO, ZnS, SnO_2 and TiO_2 are some examples of photocatalyst that have lower band gap energy and applicable for solar irradiation in photocatalysis for degradation of tons of organic effluents.

Instead of having good photoactivity, ZnO for example, has photochemical instabiliy which normally yields $Zn(OH)_2$ and Zn^{2+} upon irradiation of the ZnO particles in aqueous media [28]. Similar problem arises with CdS photocatalyst which releases Cd^{2+} ions leading to heavy metal pollution in the treated water samples. In addition, both photocatalysts suffers from the photocorrosion from self oxidation. Meanwhile, metal sulphide and α-Fe_2O_3 semiconductors also face the same problem due to photoanodic corrosion of the former and photocathodic corrosion of the latter [29]. TiO_2 on the other hand is not only highly effective for producing oxidizing species (specifically ·OH radicals which possess significant oxidation potential) but also possess other advantages that include biological and chemical stability, photo stability, non-toxicity, low cost and availability [30]. Those criteria ensure that no problems may arise upon the TiO_2 photocatalytic degradation and mineralization processes of the organic pollutants especially due to the generation of secondary pollutants.

1.4 Titanium Dioxide as photocatalyst

Titanium dioxide (TiO_2) is the most prominent semiconductor among others since TiO_2 itself satisfies the ideal photocatalyst's criteria for being relatively stable,

non-toxic (final product of harmless compound, CO_2 and H_2O) and inexpensive [31]. The band gap energy of TiO_2 of 3.2 eV (anatase) and 3.0 eV (rutile), as well as high value of refractive index (n = 2.7) make TiO_2 as an effective UV absorber and a protector of substances from UV because of rapid attenuation offered via its light absorption and scattering properties. The interaction between UV radiation and the TiO_2 surface would generate oxidative free radicals that can degrade organic contaminants [32].

TiO_2 can exist in natural crystalline forms of anatase, rutile and brookite and also artificial form (TiO_2–B, TiO_2–H) [33]. The crystallographic forms of TiO_2 determined the photoactivity of the catalyst although the quantitative differences between the rutile and anatase forms are not that transparent. It was proven that the surface recombination of the photogenerated electrons and positive holes are higher in anatase phase than in rutile phase [14]. Anatase phase in the TiO_2 crystallographic form was also reported to have good photoactivity than rutile phase although they possess similar structure of octahedral chain (TiO_2^{-6}). The reasons for this behavior could be related to the greater reflectivity for UV-visible light possesses by anatase phase though crystallite density and absorption ability of light in rutile phase is more dominant. Despite its low photoactivity, rutile form of TiO_2 has been reported to be an effective opacifier/UV protector for polymer in TiO_2 nanoparticles composites [32].

The main function of TiO_2 in the environmental photocatalysis is the photocatalytic oxidation of inorganic or organic water and air contaminants [34-35]. TiO_2 is widely used as the semiconductor that produces free radicals that can undergo reactions initiated by UV lights. The reaction is initialized when the photon energies are adsorbed by TiO_2 that results in the excitation of an electron (e^-) from

the valence band to the conduction band of the TiO_2, and leaving behind an electron vacancy hole (h^+) in the valence band. The photon has energy equal or greater than the band gap of the photocatalyst. The electron–hole pairs can either recombine or participate in chemical reactions on the surface of the photocatalyst. The ability of the pollutants molecules to be adsorbed on the photocatalyst surface will play a role on their photodegradation [35]. The mechanism of the TiO_2 reactions at the surface is given in Figure 1.2. The reactions associated with the mechanism of the charged induced reactions are provided by Equations 1.1 to 1.11.

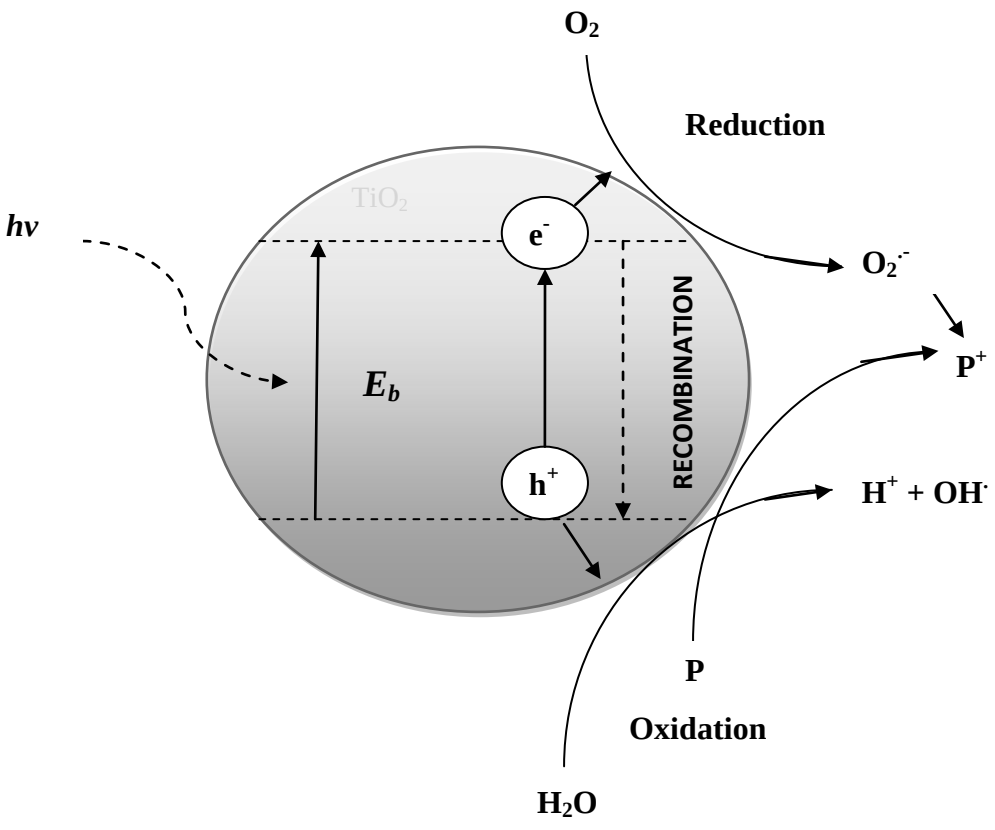

Figure 1.2: Schematic diagram of TiO_2 photocatalysis mechanism [36]

Photoexcitation: $TiO_2 + h\upsilon \rightarrow e^- + h^+$ (1.1)

Charge carrier trapping of e^-: $e^-_{CB} \rightarrow e^-_{TR}$ (1.2)

Charge carrier trapping of h^+: $h^+_{VB} \rightarrow h^+_{TR}$ (1.3)

Electron hole recombination: $e^-_{TR} + h^+_{VB}(h^+_{TR}) \rightarrow e^-_{CB}$ + heat (1.4)

Photoexcited e^- scavenging: $(O_2)_{ads} + e^- \rightarrow O_2^{\cdot -}$ (1.5)

Oxidation of hydroxyls: $OH^- + h^+ \rightarrow {}^{\cdot}OH$ (1.6)

Photodegradation by $OH^{\cdot}$:R-H + $OH^{\cdot} \rightarrow R'^{\cdot} + H_2O$ (1.7)

Direct photoholes : $R + h^+ \rightarrow R^{+\cdot} \rightarrow$ Intermediate (s)/
Final degradation products (1.8)

Protonation of superoxides: $O_2^{\cdot -} + OH^{\cdot} \rightarrow HOO^{\cdot}$ (1.9)

Co- scavenging of e^-: $HOO^{\cdot} + e^- \rightarrow HO_2^-$ (1.10)

Formation of H_2O_2 : $HOO^- + H^+ \rightarrow HO_2^-$ (1.11)

The highly reactive radicals that are formed on the surface of TiO_2 can react with the adsorbed organic pollutants resulting in the mineralization of the pollutants into harmless compounds.

1.5 Commercial TiO_2

The increasing interest on the multi-functional TiO_2 had provoked a demand in the TiO_2 production commercially where TiO_2 with commercial name such as Hombikat UV 100, PC 500 Millenium, Sigma, and Degussa P-25 (now known as Aeroxide® P-25) are currently available in the global market. Comparatively, the commercially available TiO_2 powder differed in terms of structure, particle size and surface area. Degussa P-25 had been reported to have high photoactivity due to the low recombination of electron and holes, whereas the high photoactivity in Hombikat

UV 100 TiO_2 powder is related to its fast interfacial electron transfer rate. Anyhow, the main factor that influences the physical properties is the specific production process of those catalysts that resulted in different surface concentration of active sites [37]. The same authors had investigated the influence of physical parameters of different types of TiO_2 samples on the adsorption kinetic studies of the oxalic acid. They concluded that the equilibrium behaviour of all samples was similar but differed in the measured degradation kinetic rates of the oxalic acid due to the morphological and porosity differences of the TiO_2 samples. Indeed, the geometry and chemistry of the TiO_2 samples also reflects the different level of adsorption and desorption rates of the adsorbates on the TiO_2 active surfaces. Table 1.3 below shows some available commercial TiO_2 and their respective physical properties.

Table 1.3: Commercial TiO_2 and their properties

Commercial TiO_2 / Properties	Degussa P-25	Hombikat UV100	PC500-Millenium	Sigma
Crystallographic phase	Anatase: rutile	Anatase	Anatase	Anatase
Ratio (%)	70:30, 80:20	100:0	> 99	>99
Specific area ($m^2\ g^{-1}$)	50	300	>320	9-10
Ave particle size (nm)	35	20-30	5-10	< 25
Synthesis	Flame pyrolysis of $TiCl_4$	Sulfate process, precipitation	N/A	N/A
References	[38]	[38]	[39]	[40]

In this research, TiO_2 Degussa P-25 was selected due to its versatilities towards oxidation of organic contaminants and best known as the standard material in photocatalytic field [41]. About 4428 published articles were found under the

search word: Degussa P-25 via ScienceDirect browser whereas 1150 articles were found in ISI Web of knowledge database. The reported amount of articles as shown in Figure 1.3 evidently suggested the better reputation exhibited by Degussa P-25 than other commercially available photocatalysts. As listed in the previous Table 1.3, Degussa P-25 had two crystallographic phases; anatase and rutile that are produced from the flame pyrolysis synthetic process. During the process known as Aerosil process, titanium tetrachloride, $TiCl_4$ is subjected to hydrolysis process at elevated temperatures in a vapor phase within a continuous reactor which eventually produced the nanosized TiO_2 P-25 particles [41].

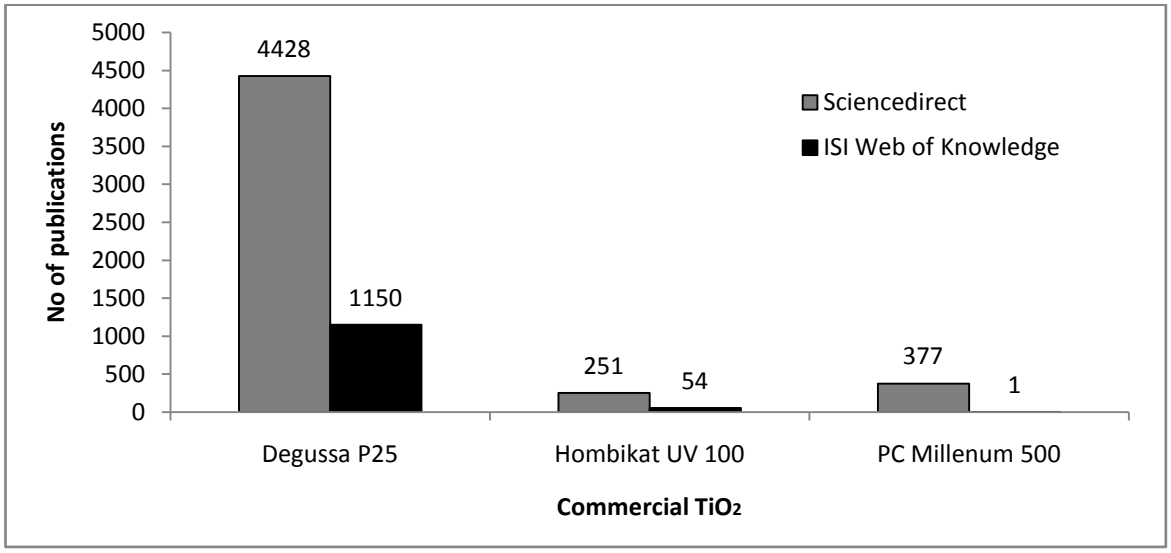

Figure 1.3: Number of publications on commercial TiO_2.
Source: Sciencedirect.com (accessed on 12.10 am 23rd May 2011)

Ohno et al. [42] had carried out investigation on the synergism between rutile and anatase TiO_2 particles in the photocatalytic oxidation of naphthalene. Enhanced photoactivity was observed when both particles were simply mixed together. They deliberately proposed that there were electrons transfer occurring

from the rutile particles (produced under high temperature and large in size) to the anatase particles (produced under low temperature and small in size). For their case with naphthalene, they suggested that the molecules were mainly oxidized on rutile particles whereas oxygen was reduced on anatase particles.

The latest article published by Ohtani and his group [43], studied the comparison on activities of the original P-25, isolated anatase and rutile particles and reconstructed P-25. They concluded that all the phases (anatase, rutile and amorphous) in P-25 behave independently which were in opposite conclusion to the Ohno's group [42] proposal on anatase-rutile interaction that had been mentioned earlier. Nevertheless, TiO_2 consisting of anatase/rutile composition in both studies showed the enhanced performance of the photocatalytic oxidation of the pollutants. However, TiO_2 Degussa P-25 and its comparative performance as the photocatalyst was not the main focus in this study. The literature reviews were purposely done to highlight the history, argument and current information on TiO_2 Degussa P-25 as the standard photocatalyst in the photocatalytic oxidation reaction. TiO_2 is used throughout this thesis as to refer to TiO_2 Degussa P-25.

1.6 Photodegradation kinetic

In general, the photodegradation of organic pollutants by TiO_2 is observed to be well fitted by first order reaction. It follows the Langmuir–Hinshelwood model, where the reaction rate is proportional to the surface coverage, according to the following equation:

$$r = \frac{dC}{dt} = \frac{1}{K_c} + K_C \qquad (1.12)$$

The above equation can be simplified to the pseudo first order kinetic equation at low concentration by integrating with respect to time, *t*.

$$\ln\left(\frac{C_o}{C}\right) = kKt = k_{app}t \qquad (1.13)$$

where;

r: the rate of phenol degradation (min^{-1});

C_o: the initial concentration of phenol (ppm);

C: the concentration of phenol at time t (ppm);

t: the irradiation time (min);

k_{app}: the reaction rate constant (min^{-1});

K: the adsorption coefficient of the phenol onto the photocatalyst particle (I/rag).

1.7 Adsorption

Adsorption is a separating process in which the adsorbates such as molecules, atoms and ions in the solvent (eg: water) are attracted to the interior and exterior surfaces of the solid namely adsorbent, on which adsorption occur through physical and chemical reactions. Generally, the adsorption of the adsorbate is influenced by pH, adsorbate concentration, size and type of adsorbents, time of interaction between the adsorbate and the adsorbent, the characteristics of the adsorbent surface and the present of the foreign substances that compete for the adsorption sites on the adsorbent. The adsorption of adsorbate onto the adsorbents can be explained by a comprehensive understanding of the nature of the interaction between the adsorbate with adsorbents for the most effective use of the adsorbent. A correlation of the

equilibrium data with the different relevant models of isotherm is essential to formulate a pragmatic program for design, operation, and optimization of the system.

The schematic diagram shown in Figure 1.4, explained the three components of adsorption process and their interactions. The main interaction force that controls the adsorption process is the affinity between the adsorbent and the adsorbate. However, the affinity between the adsorbate and the solvent (i.e. solubility) can also contribute a major role in the adsorption of adsorbate, for example; hydrophobic compounds have low solubility and tend to be 'pushed' to the adsorbent surface. Therefore, the compound is less adsorbed as opposed to the highly soluble ones.

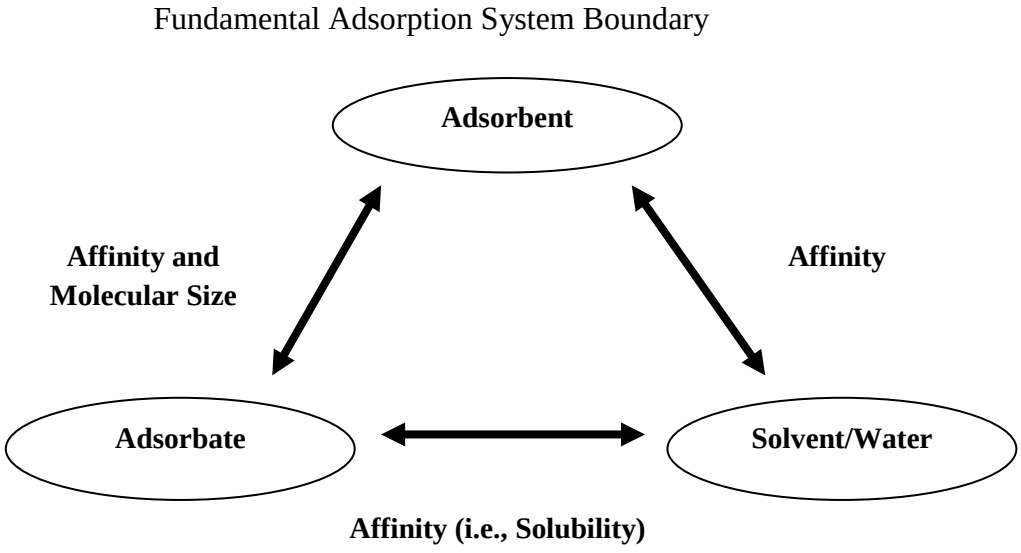

Figure 1.4: Schematic diagram of relationships between the three components of the adsorption system [44]

1.8 Activated Carbon (AC)

Adsorption by the activated carbon has been widely applied in the wastewater treatment of industrial effluents for the removal of dye, odor, organic and inorganic pollutants as well as for air pollutants. Up until now, the activated carbon is continuously being produced from various types of carbonaceous material.

Inexpensive materials such as wood, coconut shells, fruit stones, coals, lignites and petroleum coke have high carbon content and low inorganic content which are suitable for activated carbon precursors. The selection of the raw materials depends on the possibility of generating activated carbon with high adsorption capacity, density and hardness, have low inorganic matter as well as its easy availability and low in cost [45]. Some general forms of AC are shown in Table 1.4.

Table 1.4: Type of ACs and their properties [45]

Type of AC	**PAC (Powdered Activated Carbon)**	**GAC (Granular Activated Carbon)**	**ACF (Activated Carbon Fiber)**
Diameter	Less than 0.15 mm	0.5 to 2.5 mm	10 to 40 μm
Applications	Various locations in a treatment system	Fixed-bed adsorbers such as granular media filters or post filters	Fibers or as thin cloths in the treatment of gas or liquid streams at elevated flow rates
Advantages	Can interact directly with the contaminants in water	(i) Effective for adsorption of gases and vapors (ii) Has great mechanical strength	(i) Excellent mechanical properties (ii) Low thermal expansion coefficient, (iii) High thermal and electrical conductivities (iv) Low hydrodynamic resistance

According to Radovic et al. [46], the adsorption capacity of an activated carbon depends on:

a) *The nature of the adsorbent* (e.g. functional groups present, surface area and pore size distribution, ash content).

b) *The nature of the adsorbate* (e.g. functional groups present, polarity, hydrophobicity, molecular weight and size, solubility and pK, or pK, for weak electrolytes).

c) *Solution conditions* (e.g. pH, temperature and adsorbate concentration, presence of competitive solutes, polarity of solvent).

d) *Activation process* (chemical and physical activation using precursor such as $ZnCl_2$, H_2SO_4, H_3PO_4 and etc.

Generally, the porous structure of ACs consists of small amounts of chemically bonded heteroatoms (mainly oxygen and hydrogen) and in addition of mineral matter, usually ash content up to 20% of initial mass. The heterogeneity of ACs surfaces are normally associated with the geometrical and chemical sources in which the former is affiliated with the differences in size and shape of pores, cracks, pits and some steps while the latter is a contribution of different functional groups at the edges of the turbo static crystallites as well as other surface impurities. The impurity that was adsorbed on activated carbon was mainly dispersed by Van der Waals's forces. The pores in AC are classified based on their origin, size and state. Table 1.5 defines this classification.

Table 1.5: Classification of AC pores [47]

Class of pores	**Type of pores**	**Shape of pores**
Origin-based	Intraparticle pores	Intrinsic intraparticle pores Extrinsic intraparticle pores
	Interparticle pores	Rigid interparticle pores Flexible interparticle pores
Size-based	Micropores < 2 nm Mesopores 2-50 nm Macropores > 50nm	Ultramicropores < 0.7 nm Supermicropores 0.7-2 nm

State-based	Open pores Closed pores	(Latent pores)

Due to the chemical nature of activated carbon, its affinity towards polar molecules such as water and molecules of nitrogen or oxygen at room temperature is very low. However, for non-polar organic molecules, its affinity is high. For activated carbon to play its role efficiently, the internal surface area must be large enough, usually (500-1500 m^2 g^{-1}), to be accessible to the adsorbing molecule. In general, knowledge in surface area of the carbon materials is essential since the physiochemical properties of carbons are strongly influenced by the chemical species on the surface of AC. The oxygen-containing functional groups of carbon determine the acidic and basic characteristics of the adsorbent with the former usually are formed via oxidative treatment while the latter are formed from the decomposition of the acidic groups (i.e., carboxylic acid, lactone and phenol group) heated at high temperatures. Other carbon surface chemical reactions may also involve nitrogen-, hydrogen- sulphur-, phosphorus-, halogens and boron-containing functionalities [48].

There are many methods of producing activated carbon whereby thousands of them have been patented and registered worldwide. All of these production methods can be classified into two distinguished groups: thermal (physical) activation and chemical activation. The thermal activation generally consists of two steps which are carbonization of the raw material at medium or high temperatures to produce a char and activation step where the remaining char is partially oxidized in direct fired furnaces. If both steps are simultaneously carried out, the process is called direct activation. The chemical activation on the other hand, is carried out in a single carbonization stage where the raw material is impregnated with chemical agent (mostly used H_3PO_4, $ZnCl_2$ and alkaline hydroxides). The product is washed to

remove any excess chemical agent after carbonization. Figure 1.5 shows the basic flow sheet of activation processes of activated carbon.

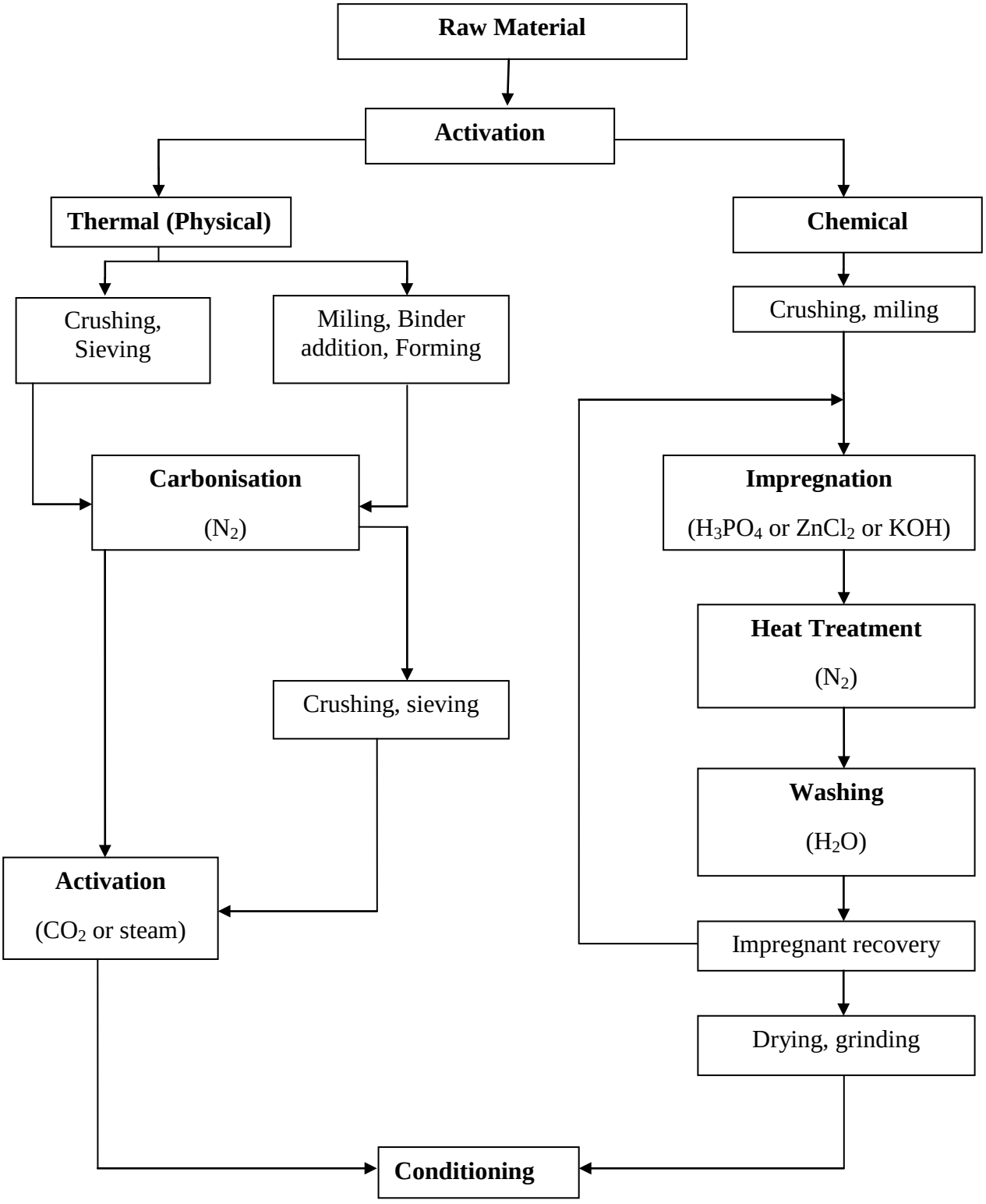

Figure 1.5: Basic flow sheet for activation of activated carbon [49]

1.9 Adsorption kinetic

The investigation on the kinetic that governs an adsorption system as well as the rate determining step is crucial for designing a large scale adsorption system. In order to elucidate the mechanism of adsorption and potential rate controlling steps such as mass transport and chemical reaction processes, a few kinetic models have been proposed to fit the experimental data. Three common kinetic models that generally used in adsorption studies are pseudo first order, pseudo second order and intraparticle diffusion.

1.9.1 Pseudo first order [50]

Lagergren's pseudo first order equation is represented as follows;

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \qquad (1.14)$$

After integration and applying boundary conditions at t=0 to t= t and qt=0 to qt=qt, the equation becomes;

$$\log (q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) t \qquad (1.15)$$

where q_e and q_t are the adsorption capacity at equilibrium (mg g^{-1}) and at time (t), respectively and k_1 is the rate constant of pseudo-first order sorption (min^{-1}). A straight line plot of log (q_e-q_t) against time (t) will give k_1 and q_e from the slope and intercept, respectively.

1.9.2 Pseudo second order

For second order adsorption mechanism where chemisorption is the rate controlling step, the equation is expressed as;

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (1.16)$$

For which after integration, the equation becomes,

$$\frac{t}{qt} = \frac{1}{k^2 q_e^2} + \left(\frac{1}{q_e}\right)t \quad (1.17)$$

Where k_2 is the rate constant of pseudo-second order (g $mg^{-1}min^{-1}$). A straight line plot of log t/q_t against time (t) will give k_2 and q_e from the slope and intercept, respectively.

1.9.3 Intraparticle diffusion

Initial adsorption generally occurs on the surface of the adsorbent whereby there is a possibility of the adsorbate to diffuse into the interior pores of the adsorbent [51]. In 1962, Weber and Morris proposed an intraparticle diffusion model which is based on an empirically found function relationship (in adsorption process), where uptake varies almost proportionally with $t^{1/2}$ rather than the contact time t. The equation is shown in equation 1.18.

$$q_t = k_d t^{1/2} + C \quad (1.18)$$

where k_d (mg g^{-1} $h^{t/2}$) is the intraparticle diffusion rate constant and is calculated by plotting q_t versus $t^{1/2}$.

1.9.4 Elovich model

This model is mainly applicable to chemisorption kinetics in the systems in which the adsorbing surface is heterogeneous [52]. The Elovich model is presented as

$$\frac{dq_t}{dt} = \alpha e^{-\beta q t} \qquad (1.19)$$

Integrating this equation for the boundary conditions, gives

$$q_t = \frac{1}{\beta} \ln (\alpha\beta) + \frac{1}{\beta} \ln t \qquad (1.20)$$

where, α = the initial adsorption rate (mg/ g min) and β = surface coverage and activation energy for chemisorptions (g/mg). The graph is calculated by plotting q_t versus ln t.

1.10 Combination of photocatalysis and adsorption processes as a single system

To date, most of the studies had successfully followed Langmuir Hinshelwood kinetic model which described the photocatalytic degradation of the respective pollutants. However, in the novel TiO_2/AC/ENR_{50}/PVC bilayer system, the ln C_o/C_e may not give good agreement with the pseudo first order linearised equation (linear regression values of $r^2 < 0.9$) due to the influence of the adsorption process on the overall removal rate of the pollutant. Since most of the adsorption processes follow pseudo second order kinetics, so, for this study, the involving a bilayer system of TiO_2/AC/ENR_{50}/PVC, evaluation of the kinetics should be evaluated also on the pseudo second order kinetic rate equation.

The second order kinetic was based on the simultaneous process i.e, photocatalysis by TiO_2 layer and adsorption by AC layer, on the removal of phenol that occurred in the bilayer system. Under the experimental conditions, there were a few assumptions which have to be considered in following the second order kinetic models such as;

1. The adsorption of phenol by activated carbon should be the dominant process as compared to the TiO_2 photocatalysis.

2. The occurrence of the two processes, photocatalysis and adsorption occur simultaneously.

Under the second order reaction, the equation becomes,

$$\frac{1}{C} = \frac{1}{C_o} + k_{app}t \qquad (1.21)$$

Equation 1.21 can be rearranged to give equation 1.22,

$$\frac{1}{C_o} - \frac{1}{C} = k_{app}t \qquad (1.22)$$

where, a graph of 1/ C versus t is plotted to obtain the slope of the graph which represents the pseudo second order apparent kinetic rate constant where the unit will be in M min^{-1}.

1.11 The equilibrium adsorption isotherm models

The adsorption of adsorbate onto the adsorbents needs a comprehensive understanding of the nature of the interaction between the adsorbate with adsorbents

for the most effective use of the adsorbent. Therefore, the equilibrium adsorption isotherm theories were developed in order to understand the mechanisms of the system and the fundamental interaction between the solutes (adsorbates) and the adsorbent in an adsorption system [53]. The adsorption process of adsorbate into the adsorbent can be explained by using several models of the equilibrium isotherms which are listed in Table 1.5. Among them are the two most popular models namely Langmuir and Freundlich models. The two models are usually used in the adsorption of solid-liquid system. Initially, the adsorption capacity which was the amount of adsorption at equilibrium is computed as follows:

$$\text{Adsorption capacity } (q_e) = \left(\frac{\text{Co-Ce}}{\text{W}}\right) \text{V} \qquad (1.23)$$

C_o= initial adsorbate concentration

C_e = final or equilibrium concentration of adsorbate (mg/L)

W = weight of the adsorbent (g)

V = volume of the adsorbate solution (mL)

However, despite of the two famous isotherm models, there are some other models which were introduced later in order to understand the adsorption mechanism that failed to be explained by the former two models. They were Temkin, Brunauer-Emmett- Teller (BET), Dubinin-Radushkevich (D-R) and Elovich isotherms. The equations fitted for each model are given in Table 1.6. The details of the isotherm models are also provided in Table 1.6.