

**POLYANILINE MODIFIED MAGNETIC  
NANOPARTICLES COATED WITH DICATIONIC  
IONIC LIQUID FOR THE REMOVAL OF RHODAMINE  
B AND EXTRACTION OF POLYCYCLIC AROMATIC  
HYDROCARBONS**

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RHODAMINE B AND EXTRACTION OF  
POLYCYCLIC AROMATIC HYDROCARBONS**

by

**MOHAMAD SHARIFF BIN SHAHRIMAN**

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## LIST OF ABBREVIATIONS

ACE	Acenaphthalene
ACN	Acetonitrile
BET	Brunauer Emmelt Teller
BJH	Barret–Joyner–Halenda
C	Carbon
CHN	Carbon, hydrogen and nitrogen
CNTs	Carbon nanotubes
CTAB	Cetyl trimethylammonium bromide
DCM	Dichloromethane
DICAT	Dicationic ionic liquid
D-R	Dubinín-Radushkevich
EF	Enrichment factor
EtOH	Ethanol
EU	European Union
FFA@MNP	Free fatty acid@magnetic nanoparticles
FLA	Fluoranthene
FLU	Fluorene
G	Graphene
GC-FID	Gas chromatography – flame ionization detector
GC-MS	Gas chromatography mass spectrometry
Hr	Hour
HPLC	High performance liquid chromatography
ICP-MS	Inductively coupled plasma mass spectrometry
ILs	Ionic liquids
JCPDS	Joint Committee on Powder Diffraction Standards

LC-MS	Liquid chromatography – mass spectrometry
LLE	Liquid-liquid extraction
LOD	Limit of detection
LOQ	Limit of quantification
MeOH	Methanol
MIPs	Molecular imprinted polymers
MNPs	Magnetic nanoparticles
MSPE	Magnetic solid phase extraction
MWCNT	Multiwall carbon nanotubes
N	Nitrogen
NA	Not available
ND	Not detected
NMR	Nuclear magnetic resonance
PA	Polyacetylene
PAHs	Polycyclic aromatic hydrocarbons
PANI	Polyaniline
PHE	Phenanthrene
PPP	Polyparaphenylene
PPV	Polyphenylene vinylenes
PPY	Polypyrroles
PTH	Polythiophenes
PYR	Pyrene
R	Recovery
RB	Rhodamine B
RSD	Relative standard deviation
SD	Standard deviation



SEM	Scanning electron microscope
SIM	Selective ion monitoring
SPE	Solid phase extraction
SPME	Solid phase microextraction
TEM	Transmission electron microscope
TGA	Thermo gravimetric analysis
USEPA	United States Environmental Protection Agency
UV-Vis	Ultraviolet–visible spectroscopy
VSM	Vibration sample magnetometer
XRD	X-ray powder diffraction

## LIST OF SYMBOLS

B	Rate of adsorption	L/mg
$b_T$	Temkin constant of heat of adsorption	J/mol
C	Intercept	mg/g
$C_e$	Equilibrium concentration of solutions	mg/L
$C_o$	Initial concentration of solutions	mg/L
$\text{cm}^3/\text{g}$	Pore volume	-
E	Mean free energy	kJ/mol
$\text{Fe}^{2+}$	Iron(II) oxide	-
$\text{Fe}^{3+}$	Iron(III) oxide	-
$\text{Fe}_3\text{O}_4$	Magnetite	-
$\text{H}_2\text{O}$	Water	-
K	Kelvin	-
K	Intra particle diffusion rate constant	mg/g min
$k_l$	Rate constant of pseudo first order model	$\text{min}^{-1}$
$k_d$	Equilibrium constant	$\text{m}^3/\text{mol}$
$k_{\text{ext}}$	Diffusion rate parameter	1/min
$K_F$	Adsorption capacity	$\frac{(\text{mg/g})}{(\text{L/mg})^{1/n}}$
$K_T$	Temkin constant of equilibrium binding energy	L/mg
$\text{m}^2/\text{g}$	Surface area	-
$n_f$	Ability of the adsorption process	
Nm	Nanometer	-
OH	Hydroxide	-
$q_m$	Langmuir consistent identified with the adsorption limit	mg/g
$q_t$	Amount of solute adsorbed	mg/g

R	Universal gas constant	$\text{kJ}/(\text{molK})$
$R_L$	Dimensionless separation factor	
$R^2$	Coefficient of determination	-
$\text{SiO}_2$	Silicon dioxide	-
T	Temperature	K
V	Volume of the solution	L
W	Mass of the dry adsorbent used	g
A	Underlying sorption rate	$\text{mg}/\text{g min}$
B	Adsorption energy constant	$\text{mol}^2/\text{kJ}^2$
B	Expanded surface coverage	$\text{g}/\text{mg}$
$\varepsilon$	Polanyi potential	-
$\Delta G^\circ$	Change of free energy	-
$\Delta H^\circ$	Change of enthalpy	-
$\Delta S^\circ$	Change of entropy	-

**POLIANLINA DIUBAHSUAI DENGAN MAGNET NANOZARAH DISALUTI  
DENGAN CECAIR IONIK DWIKATION UNTUK PENYINGKIRAN  
RHODAMIN B DAN PENGEKSTRAKAN POLISIKLIK AROMATIK  
HIDROKARBON**

**ABSTRAK**

Dalam kajian ini, magnet nanozarah (MNPs) sebatian nano diubahsuai dengan polianlina (PANI) disaluti dengan cecair ionik dwikation (DICAT) yang baru berjaya disintesis untuk menjadikan MNP-PANI-DICAT sebagai bahan generasi baru untuk pengekstrakan fasa pepejal magnet (MSPE). Bahan yang disintesis diklasifikasikan dengan menggunakan beberapa teknik seperti analisis FT-IR, NMR, CHN, VSM, XRD, TGA, BET, SEM dan TEM. TEM mendedahkan bahawa peningkatan pengagihan saiz diameter zarah daripada MNPs (4.6 nm), MNP-PANI (5.0 nm) kepada MNP-PANI-DICAT (6.8 nm). Sehubungan itu, luas permukaan untuk analisis BET menurun daripada  $96.9 \text{ m}^2 \text{ g}^{-1}$  dalam MNP kepada  $45.2 \text{ m}^2 \text{ g}^{-1}$  dalam MNP-PANI-DICAT. Keputusan analisis TGA menunjukkan bahawa kehadiran IL meningkatkan kestabilan MNP-PANI-DICAT berbanding dengan MNP-PANI dan MNP. Kajian penyerapan awal dengan menggunakan MNP-PANI-DICAT menunjukkan kapasiti penyerapan yang baik dan kadar penyerapan yang cepat untuk proses penyingkiran Rodamin B (RB) di dalam sampel air. Beberapa parameter penyingkiran telah dioptimumkan. Penyingkiran di dapati bergantung kepada julat. Oleh itu, julat 1 dipilih untuk proses penyerapan RB disebabkan penyingkiran optimum telah dilihat di julat ini. Analisis kinetik telah dilakukan dan hasilnya menunjukkan bahawa MNP-PANI-DICAT paling sesuai dengan persamaan pseudo- tertib kedua untuk penyerapan RB dengan nilai  $R^2$  di antara 0.9992 hingga 1. Bagi kajian isoterma, model Temkin telah

di dapati bersesuaian dengan isoterma untuk penyerapan RB pada MNP-PANI-DICAT. Sebanyak 94.7% diperolehi daripada penyingkiran RB oleh MNP-PANI-DICAT pada keadaan yang optimum. Selain itu, keputusan hasil termodinamik menunjukkan nilai negatif  $\Delta G^\circ$  pada penyerapan RB, yang menjelaskan bahawa proses itu boleh dilaksanakan secara termodinamik, spontan dan kimia pada suhu yang rendah. Proses entalpi ( $\Delta H^\circ$ ) juga menunjukkan nilai negatif (-40.41) menjelaskan bahawa penyerapan RB adalah proses eksotermik. Selain itu, kaedah baru ini digunakan sebagai penyerap magnet untuk kepekatan dan pemisahan polisiklik aromatik hidrokarbon (PAHs). Lima jenis PAHs dikaji seperti acenaftena (Ace), pirena (Pyr), fluorena (Flu), fluorantena (Fla) dan phenanterena (Phe) di mana ia diekstrak dengan menggunakan penyerap MNP-PANI-DICAT dalam kaedah MSPE. PAHs dikesan dengan menggunakan gas kromatografi - spektrometrik jisim (GC-MS). Berdasarkan keadaan optimum, kaedah yang dicadangkan dinilai dan digunakan untuk analisis PAH di dalam sampel persekitaran. Kaedah pengesanan menunjukkan garis lurus yang baik ( $0.005 - 500 \mu\text{g L}^{-1}$ ) dengan nilai  $R^2 > 0.999$ . Had pengesanan (LOD) dan kuantifikasi (LOQ) terhadap kaedah yang dibangunkan (MNP-PANI-DICAT-MSPE) masing-masing berada dalam lingkungan  $0.0008 - 0.2086 \mu\text{g L}^{-1}$  dan  $0.0024 - 0.6320 \mu\text{g L}^{-1}$ . Pemulihan pengekstrakan air, enapcemar dan sampel tanah di antara 80.2 - 111.9% dengan ketepatan yang gitu dari sisihan piawai relatif (RSD) yang kurang daripada 5.6%. MNP-PANI-DICAT yang baru disintesis mempunyai kepekatan yang baik, kebolehgunaan semula dan pantas pengekstrakan untuk PAH di bawah prosedur MSPE di dalam pelbagai sampel persekitaran.

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**ABSTRACT**

In the present study, magnetic nanoparticles (MNPs) nanocomposites modified with polyaniline (PANI) coated with newly synthesized dicationic ionic liquid (DICAT) forming MNP-PANI-DICAT were successfully synthesized as a new generation material for magnetic solid phase extraction (MSPE). The synthesized materials were characterized using few techniques such as FT-IR, NMR, CHN, VSM, XRD, TGA, BET, SEM and TEM analysis. TEM revealed that particles size diameters distribution increased from MNPs (4.6 nm), MNP-PANI (5.0 nm) to MNP-PANI-DICAT (6.8 nm). While, the surface area of BET analysis decreases from 96.9 m<sup>2</sup> g<sup>-1</sup> in MNPs to 45.2 m<sup>2</sup> g<sup>-1</sup> in MNP-PANI-DICAT. TGA analysis results showed that the presence of ionic liquids (ILs) increased the stability of the MNP-PANI-DICAT compared to MNP-PANI and native MNP. Preliminary sorption study of MNP-PANI-DICAT showed extraordinary adsorption capacity and fast adsorption rates for removal of Rhodamine B (RB) in water samples. Several removal parameters have been optimized and the removal process was found to be pH dependent (pH 1). The adsorption kinetic was investigated and result showed MNP-PANI-DICAT was best fitted in pseudo-second order for the adsorption of RB with coefficient of determination (R<sup>2</sup>) value ranged from 0.9992 to 1. In isotherm studies, Temkin's model was found to fit well with the adsorption isotherm of RB on MNP-PANI-DICAT. The percentage removal of RB was found to be 94.7% by MNP-PANI-

DICAT under optimized condition. Moreover, the thermodynamics results showed negative values of  $\Delta G^\circ$  for the adsorption of RB, which indicated that the process is thermodynamically feasible, spontaneous and chemically controlled at lower temperature. The negative value of enthalpy  $\Delta H^\circ$  (-40.41) indicated that the adsorption was an exothermic process. On the other hand, MNP-PANI-DICAT was being applied as magnetic adsorbents for pre-concentration and separation of five polycyclic aromatic hydrocarbons (PAHs), namely, acenaphthalene (Ace), pyrene (Pyr), fluorene (Flu), fluoranthene (Fla) and phenanthrene (Phe). Under the optimal conditions, the proposed method was evaluated and applied to the analysis of PAHs in environmental samples using gas chromatography-mass spectrometry (GC-MS). The validation method showed good linearity (0.005 - 500  $\mu\text{g L}^{-1}$ ) with coefficient of determination ( $R^2$ ) > 0.999. The limit of detection (LOD) and quantification (LOQ) of the developed method (MNP-PANI-DICAT-MSPE) were in the range of 0.0008 – 0.2086  $\mu\text{g L}^{-1}$  and 0.0024 – 0.6320  $\mu\text{g L}^{-1}$  respectively. The extraction recoveries of environmental water, sludge and soil samples were ranged from 80.2 – 111.9% with admirable precision of relative standard deviation (RSD) which is less than 5.6%. The newly synthesized MNP-PANI-DICAT owned with good sensitivity, reusability and fast extraction of PAHs under the MSPE procedure in various environmental samples.

## CHAPTER 1

### INTRODUCTION

#### 1.1 General background

Recently nano-sized materials, magnetic separation techniques have attracted enormous attention in among scientific research in various fields due to their unique sizes as well as physic-chemical properties (Bruce & Sen, 2005; Larsen et al., 2009). A part of that, magnetite ( $\text{Fe}_3\text{O}_4$ ) nanoparticles showed outstanding performance in term of superior superparamagnetic property, good compatibility, less toxicity and greater of physicochemical stability (Gupta & Gupta, 2005).

Magnetic nanoparticles (MNPs) have gain enormous interest in various fields and applications since emerging as an innovative compound due to characteristics (Bruce & Sen, 2005; Larsen et al., 2009). Owing to the unique magnetic, biocompatibility properties and high surface area, MNPs have a wide-range in various potential applications such as catalyst, biomedical and analytical methods (Gill et al., 2007; Du et al., 2012). The target analytes can be separated by an external magnetic field from aqueous sample during the extraction process.

However, the application of MNPs in extraction process is challenging because it can be easily oxidized and agglomerate in aqueous solution. Therefore, some modifications on the surfaces of MNPs either by functionalization or coating with other solid support or functional group such as natural, conductive and synthetic polymers is necessary for better resolution and extraction efficiency (Xia et al., 2010).



Numerous conducting polymers such as natural polymers include chitosan, dextran, gelatin, starch, cyclodextrin etc. While, synthetic polymers include polythiophene, polypyrrole, polyaniline, polyphenylene and polyacetylene which have been comprehensively discovered in scientific.

Moreover, ionic liquids (ILs) have been used lately among researchers in order to increase the extraction efficiencies by loading on the surface of the polymers that gained an interesting impact in research. It can be classified as salts due to its behaviours that melt at or below 100°C (Anderson et al., 2006; Raoov et al., 2013b). Moreover, ILs are known as unique solvent which commonly being used in extraction, synthesis and electrochemistry studies. The significant benefits of using ILs as coating materials are to improve the selectivity and sensitivity toward the targeted analytes (Yao et al., 2009; Zhao et al., 2009), by increasing the hydrophobicity and  $\pi$ - $\pi$  interactions between analytes and the sorbent coating (Meng & Anderson, 2010).

To the best of our knowledge, monocationic ionic liquid has been extensively studied since few decades ago, but dicationic ionic liquid is less and lack reported. Dicationic ionic liquids are more suitable materials as advanced electrolyte materials applications (McEwen et al., 1999; Endres & El Abedin, 2006; Galiński et al., 2006; Seki et al., 2006). In dicationic ionic liquid form, dication is associated with two identical anions, which makes it either exist in hydrophilic or hydrophobic state toward aqueous solution. Moreover, ionic liquid can be classified as symmetric (combination of two identical monocations) or asymmetrical (combination of two different monocations) structures. Other than the uniqueness such as high thermal ability, a wide temperature range of liquid state, and biological activities (Chinnappan & Kim, 2012), the ability of functionalization of dicationic ionic liquids gives the possibility of designing more structures with respect to cations, anions and the length of chain

linking two cations based on imidazolium and pyrrolidinium. (Jadhav & Kim, 2012). However, the application of this type of magnetic material in magnetic solid phase extraction (MSPE) is still at its early stages. MSPE is very convenient method which use sorbent MNPs as core materials coating or loading with different chemical groups or polymer to act as an extracting agent. It will disperse in aqueous solution to adsorb target analytes and the sorbent was isolated easily by external magnetic field without passes through the centrifugation and filtration and also consumption low of organic solvents.

Therefore, in this work, by combining the excellent properties of MNP, PANI and ILs, we decided to coat new type of dicationic ILs onto the surfaces of MNP-PANI to produce a new generation of material (MNP-PANI-DICAT) which acts as an adsorbent in magnetic solid phase extraction (MSPE) in batch adsorption study of dye and extraction of PAHs from the various environmental matrices since the synthesis of dicationic ionic liquid with polyaniline coated  $\text{Fe}_3\text{O}_4$  has not been reported yet in any studies.

## **1.2 Problem statement**

Since last decades, there are many sample pre-treatment techniques such as solid phase extraction (SPE), microextraction and liquid-liquid extraction (LLE) which have been established by researchers. However, there is still a need to explore a more applicable method that give greater recovery, less maintenance, less solvent and easy separation in aqueous solution. In this study, magnetic nanoparticles have been introduced into SPE turning out to be a simple sample pre-treatment technique known as magnetic solid phase extraction (MSPE) that was accredited to give high enrichment factor toward various types of analytes. MSPE is considered as the most advanced technique in term of extraction and adsorption of analytes since it can increase the enrichment factor toward the environmental samples compared to conventional SPE methods. Therefore, in this study, new generation material of MNP-PANI-DICAT will be introduced as an adsorbent for the removal of dye and MSPE of aromatic compounds.

## **1.3 Objectives of the research**

This study boarded on the subsequent purposes:

1. To synthesize the magnetic nanoparticles (MNPs) modified with polyaniline coated with dicationic ionic liquid (MNP-PANI-DICAT) and characterize while, compare stability properties of the MNP-PANI-DICAT with native MNPs and magnetic polyaniline polymer (MNPs-PANI).
2. To optimize and compare the parameters of batch adsorption studies such as the effect of pH, contact time, concentration and temperature by newly synthesized MNPs-PANI-DICAT for the removal of rhodamine B (RB) from aqueous solutions.

3. To develop, optimize and validate the parameters by using MNP-PANI-DICAT as an adsorbent for magnetic solid phase extraction (MSPE) method for the extraction of polycyclic aromatic hydrocarbons (PAHs) from environmental samples.

#### **1.4 Scope of study**

This study involved the synthesis of MNP-PANI-DICAT polymer and characterization by Fourier Transform-Infrared (FT-IR), Nuclear Magnetic Resonance (NMR), X-ray power Diffraction (XRD), Thermo Gravimetric Analysis (TGA), Brunauer-Emmett-Teller (BET) and morphological analysis by Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM). Preliminary batch adsorption study was carried out to evaluate the performance of MNP-PANI-DICAT for the removal of rhodamine B in aqueous solution and being compared with native MNPs and MNP-PANI. Furthermore, this developed MNP-PANI-DICAT was used as an adsorbent to extract PAHs from environmental samples using GC-MS.

#### **1.5 Organization of the thesis**

The present thesis is organized into five chapters. Chapter 1 briefly introduced the magnetic nanoparticles with separation procedure, polymerization of aniline polymer and the novelty of dicationic ionic liquid (DICAT). Besides, this chapter also covered the problem statement, objectives and structural organization of the whole thesis. Chapter 2 presented a literature review for the magnetic nanoparticles, polyaniline, ionic liquids, extraction method and properties of analytes that being used in this study. Chapter 3 focuses on the methodology which consists of three parts: part

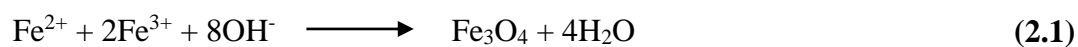
I (synthesis and characterization techniques), part II (batch adsorption studies of RB) and part III (application of MSPE procedure of PAHs). Chapter 4 mainly highlights on the results and discussion that are divided into three parts: part I (characterization results), part II (batch adsorption studies of RB) and part III (application of MSPE procedure of PAHs). Conclusions along with recommendations are written in Chapter 5.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Magnetic nano-particles (MNPs)

The special and greater properties of nanomaterial have fascinated much attention in the past two decades. Magnetic nanoparticles (MNPs) have gain enormous interest in various fields and applications since it can develop as a new catalyst chains because of their particular characteristics (Bruce & Sen, 2005; Larsen et al., 2009). Due to their high surfaces area, biocompatibility, distinctive magnetic properties, it has wide-ranging of potential uses in catalyst support and biomedical applications (Gill et al., 2007; Du et al., 2012). In the last decades, many synthesis methods have been established to synthesize iron oxide nanoparticles. The chemical co-precipitation method may be the most encouraging one because of its simplicity and yet high productivity. In general, the overall reaction of MNPs procedure written as follows (Schwertmann & Cornell, 2008):



Summary of MNPs coated with other materials are shown in **Table 2.1**.

**Table 2.1:** Summary of coating of MNPs with other materials to extract targeted analytes

<b>Magnetic materials coating</b>	<b>Targeted analytes</b>	<b>Matrix</b>	<b>Technique</b>	<b>Reference</b>
SiO <sub>2</sub> /C <sub>18</sub>	PAHs	Tap water samples	GC-MS	(Liu et al., 2009)
OPA	PAHs	Tap, lake water and hospital sewage samples	GC-MS	(Ding et al., 2010)
SiO <sub>2</sub> /G	PAHs	Tap, reservoir and sea water samples	HPLC-FLD	(Wang et al., 2013)
Fatty acid	PAHs	Sewage sludge and landfill leachates	HPLC-DAD	(Rozi et al., 2016)
Cyano-ILs	PAHs and chlorophenols	Leachate and sludge samples	HPLC-DAD	(Bakhshaei et al., 2016a)
Polythiophene (P3TArH)	Phthalates	Bottled mineral and fresh milk samples	GC-FID	(Baharin et al., 2016)
CTAB	Amaranth	River water samples	Spectrophotometric detection	(Zargar et al., 2009)
Polydopamine	Amaranth, Ponceau 4R, sunset yellow and allure red	Beverage samples	HPLC-UV	(Chai et al., 2016)

**Table 2.1** (continued)

Poly(DVB-co-MAA)	Phenols	Sewage influents, tap and sea water samples	LC-MS/MS	(Li, Lam, et al., 2010)
Chitosan@PANI	Phenols	Environmental and juice samples	HPLC	(Jiang et al., 2015)
PANI	Methylmercury	Sea water samples	GC-MS	(Mehdinia et al., 2011)
SiO <sub>2</sub> /C <sub>18</sub>	Diazinon and fenitrothion	Groundwater samples	HPLC-UV	(Maddah & Shamsi, 2012)
Carbon	Organophosphorus pesticides (OPPs)	Well, tap, river and mineral water samples	HPLC-UV	(Heidari & Razmi, 2012)
G/CNTs	Oxytetracycline	Sewage water sample	HPLC-UV	(Sun et al., 2015)
IJMS/C <sub>18</sub>	Sudan dyes	River and surface water samples	UFLC-UV	(Jiang et al., 2012)
MIPs	Sulfonamides	Duck feed and chicken feed samples	HPLC-UV	(Kong et al., 2012)
MHNTs@MIP	2,4-Dichlorophenoxyacetic acid	Lake and river water samples	HPLC-UV	(Zhong et al., 2014)
Humic acid	Rhodamine B	Water samples	UV-Vis Spectrophotometer	(Peng et al., 2012)

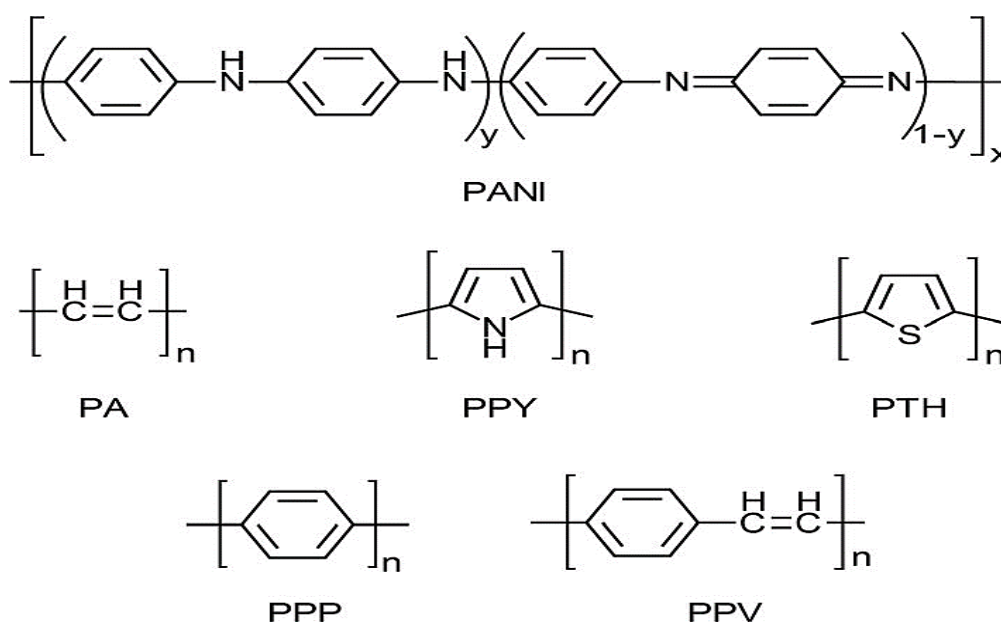


**Table 2.1** (continued)

ILs-[C <sub>6</sub> MIM][Br]	Reactive red-120 and 4-(2-pyridylazo)	Aqueous solutions	UV-Vis Spectrophotometer	(Absalan et al., 2011)
Graphene nanosheet (GNS)	Methylene blue	Aqueous solutions	UV-Vis Spectrophotometer	(Ai et al., 2011)

## 2.2 Aniline polymers (PANI)

Polyaniline was initially discovered in early of 1834, and it was referred as aniline black. Following this, Letheby carried out research to analyse this material in 1862. PANI is known as a mixed oxidation state polymer composed of reduced benzoid units and oxidized quinoid units (Shimano & MacDiarmid, 2001) and researchers discovered this as an interesting characteristic of it. Polyaniline (PANI), polyacetylene (PA), polypyrroles (PPY), polythiophenes (PTH), polyparaphenylene (PPP) and polyphenylene vinylenes (PPV) are among the most widely studied materials in the family of conducting polymers as illustrated in **Figure 2.1**. Furthermore, it was revealed that PANI had characteristics of exchanging between a conductor and an insulator under certain experimental conditions. Since then, the material has become a subject of potential interest in research. Summary of extraction and removal of polyaniline with other materials are shown in **Table 2.2**.



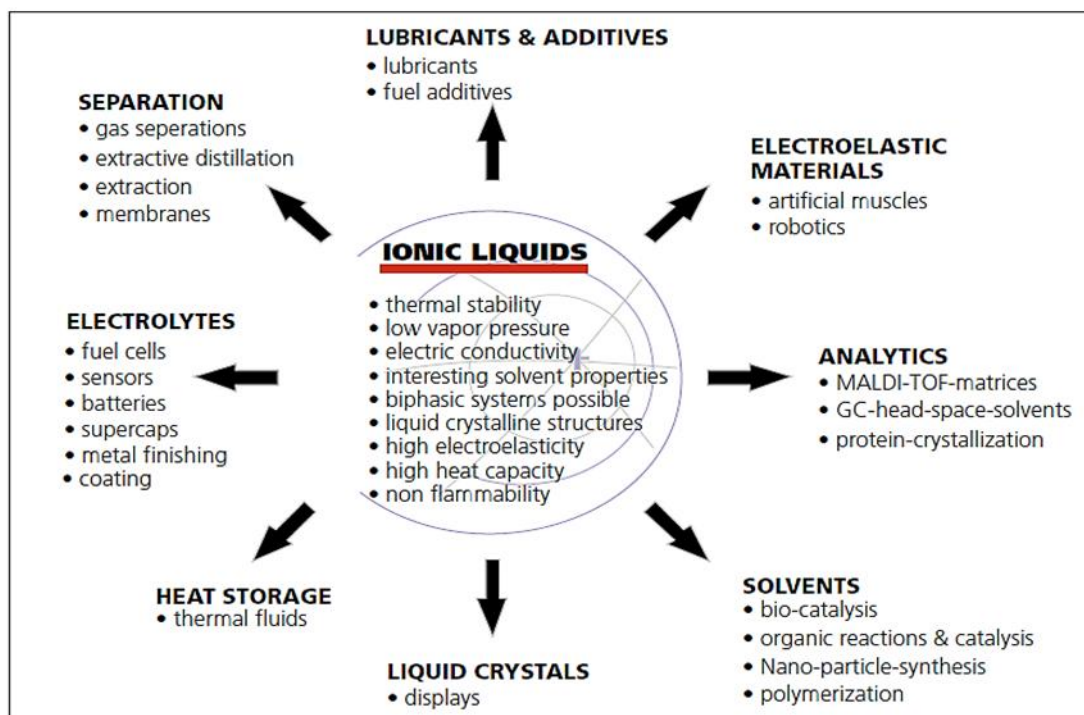
**Figure 2.1:** Chemical structure of some typical conducting polymers (Xia et al., 2010)

**Table 2.2:** Summary on extraction and removal of various pollutants using polyaniline based materials

<b>Polyaniline-based material</b>	<b>Analyte</b>	<b>References</b>
Fe <sub>3</sub> O <sub>4</sub> /PANI	Extraction-methylmercury	(Mehdinia et al., 2011)
PANI-IL	Extraction-organochlorine pesticides	(Gao et al., 2011)
Fe <sub>3</sub> O <sub>4</sub> /PANI	Extraction-benzodiazepines drugs	(Asgharinezhad et al., 2014)
PANI-IL	Extraction-different ILs	(Li et al., 2014)
Fe <sub>3</sub> O <sub>4</sub> /C/PANI	Extraction-pyrethroids	(Wang et al., 2014)
PANI-poly(propylene oxide)	Extraction-carbamate pesticides	(Ai et al., 2015)
Fe <sub>3</sub> O <sub>4</sub> @CHI@PANI	Extraction-bisphenol A, 2,4-Dichlorophenol and triclosan	(Jiang et al., 2015)
Co <sub>3</sub> O <sub>4</sub> nanocube doped PANI	Removal-Methyl orange	(Shahabuddin et al., 2016)
Pani/ Fe <sub>3</sub> O <sub>4</sub>	Removal-Reactive red 198	(Tayebi et al., 2016)

### 2.3 Ionic Liquids (ILs)

ILs can be well-defined as nonmolecular solvent which are organic cations and organic/inorganic anions. The physical and chemical properties of structure ILs can be in various state by altering the combination of anions and cations. As illustrated in **Figure 2.2**, ILs exhibit a very unique properties compared to other solvents (Sun & Armstrong, 2010).

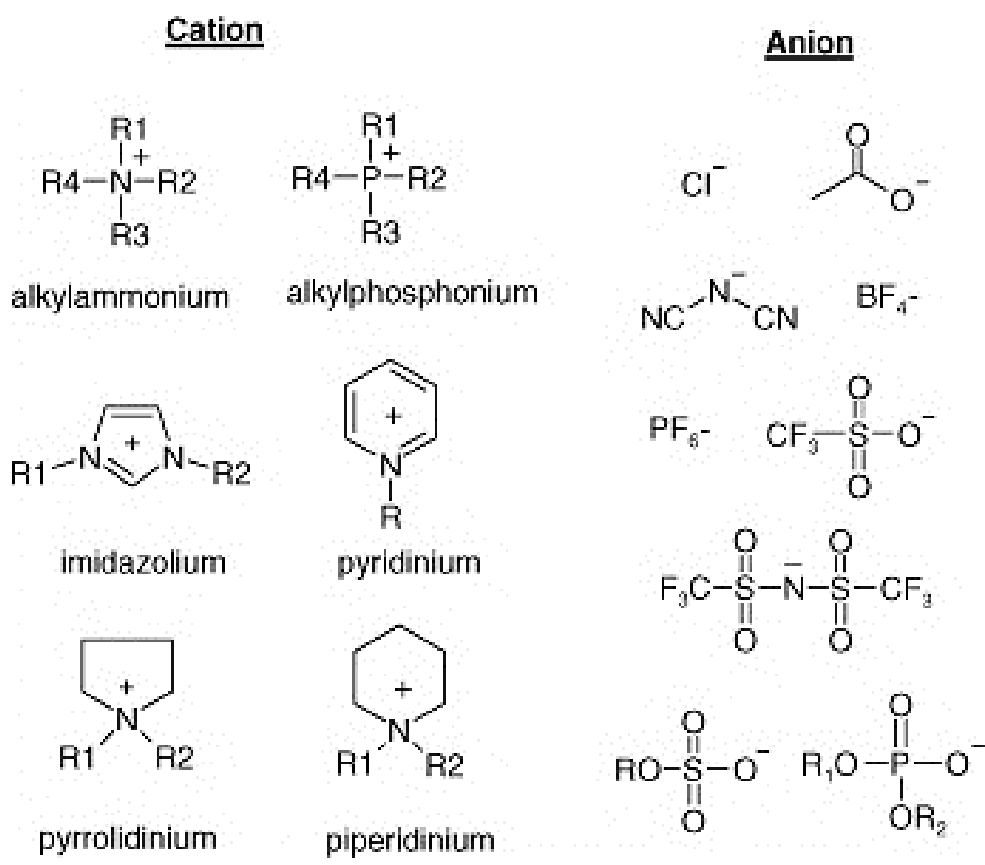


**Figure 2.2:** Properties of ILs and their potential and current applications

ILs can be useful in many applications, such as liquid phase extraction, electrochemistry, organic synthesis, and polymerization processes which make it as alternative solvents. The application of ionic liquids in extraction and separation studies have been summarized in **Table 2.3**. Alkylimidazolium-based ILs were found to be the most common ILs that applied in separation studies (Ragonese et al., 2009; Yao & Anderson, 2009). Ability of ILs in isolating polar and non-polar compounds due to enhanced selectivity performance of ILs with “dual nature”, representing that ILs might be compatible organic solvent for analytical separations. Additionally, capability of ILs mixed with other low viscosity solvents can be applied as mobile phase additives in reversed-phase chromatography (Xiaohua et al., 2004). The chemical structure of both cation and anion of ILs are shown in **Figure 2.3**.

**Table 2.3:** Applications of IL in separation sciences

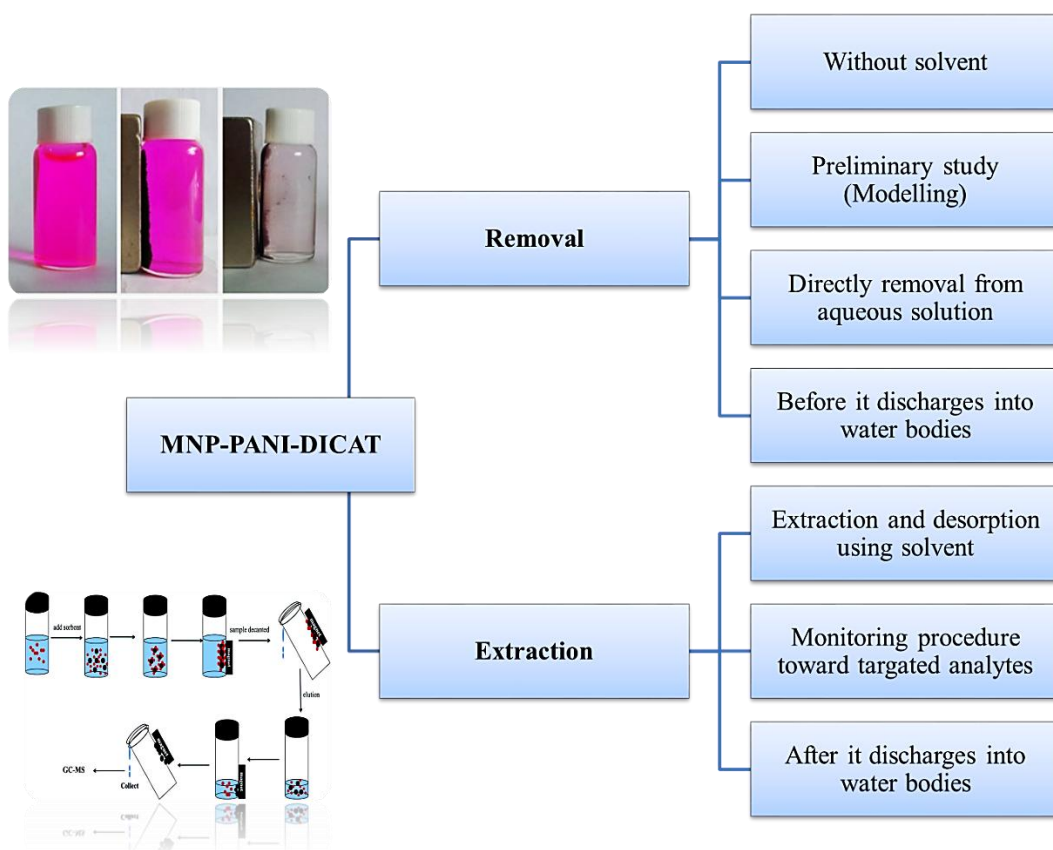
<b>Ionic liquids</b>	<b>Target compounds</b>	<b>Method of detection</b>	<b>Reference</b>
1-allyl-3-hexyl imidazolium tetrafluoroborate	Ephedrines	Separation-HPLC	(Shu Juan et al., 2004)
1-butyl-3-methylimidazoliumchloride and 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl] imide	Alcohols and aromatic compounds	Separation-GC	(Baltazar et al., 2008)
1-octyl-3-propylimidazolium chloride	Acidic, basic, neutral compounds	SFC/SFE-HPLC	(Chou et al., 2009)
1,9-di(3-vinyl-imidazolium) nonanebis (trifluoromethyl)sulfonylimidate	Fatty acid and methyl esters	SPE-GC	(Ragonese et al., 2009)
Bis[(trifluoromethyl) sulfonyl] imide	Esters	SPE-GC	(Zhao et al., 2009)
Imidazole, 1-methylidazole, 2-ethyl-4-methylimidazole	Caffeine, theophylline theobromine	Separation-HPLC	(Zhu et al., 2010)
1-butyl-3-methylimidazolium hexafluorophosphate	Organochlorine	(HS-SPME)-GC-ECD	(Gao et al., 2011)
1-benzylimidazole	Phenols and As(V)	Removal-UV-Vis and ICP-MS	(Raovv et al., 2013b)
1-benzyl-3-(trimethoxysilypropyl)imidazolium chloride	PAHs and Chlorophenols	MSPE-HPLC-DAD	(Bakhshaei et al., 2016b)
Bis(trifluoromethanesulfonyl)imide	PAHs and phthalate	SPME-GC	(Hou et al., 2016)



**Figure 2.3:** Common structure of cations and anions of ILs (Zhao & Baker, 2013)

## 2.4 Principle of removal and extraction procedure

There are two methods that involve in this study, removal and extraction techniques (Figure 2.4). Removal procedure has been developed for directly remove targeted analyte from aqueous solution before it discharges into water bodies without using organic solvents. This procedure can be applied in big scale such as industrial waste water treatments. This removal part also acts as a preliminary study on adsorption between new development material and adsorbate. For the extraction technique for development of simple pre-treatment for monitoring procedure toward targeted analytes in water bodies. This procedure involves of extraction and desorption step that use organic solvents as eluting solvent.



**Figure 2.4:** Removal and extraction procedure for new development materials

## **2.5 Adsorption**

An adsorption procedure would be the most proficient and financially practical technique for the expulsion of harmful natural contaminations. Adsorption process is by all accounts the most vital piece of partition and is utilized broadly in different fields, for example, synthetic, organic, expository, and natural fields (Raov et al., 2013a).

Analytes are adsorbate, MNP-PANI-DICAT polymer is adsorbent, and water is the transportation medium. As follows this analysis had explored the adsorption equilibrium kinetic, mechanism, and varied parameters influenced the adsorption procedure, with a specific end goal to understand the adsorption procedure to be more exact. The understanding of adsorption are useful for the designing adsorption system and to apply the polymers into adsorption application, such as waste water effluent treatment.

### **2.5.1 Adsorption kinetics**

Mostly, adsorption kinetic studies involved the rate and mass transfer pathways in between two media of solid-liquid adsorption study, mass transfer either in solution, inside the adsorbent and sorption at solid sites (Hall et al., 1966). In wastewater treatment, the vital characteristic which is adsorption kinetic study reveals the adsorbate uptake rate where the equilibrium time of the adsorbate uptake at solid-liquid interface being controlled (Dąbrowski, 2001).

Furthermore, to discover the mechanism of adsorptions, which are pseudo first and second order, Elovich's equation, internal particle diffusion and external diffusion models being used.



### 2.5.1(a) Pseudo first order model

Pseudo first order was developed (Lagergren, 1898) and extensively applied in adsorption of numerous solutes from aqueous solution onto different solid adsorbents. This kinetic equation of pseudo first order that described the adsorption of liquid-solid systems found on the solid capacity. The pseudo first order equation as listed in Equation (2.2):

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (2.2)$$

Integrating Equation (2.2) for fixed conditions,  $t=0$  to  $t=t$  and  $q_t=0$  to  $q_t=q_t$ , generates Equation 2.3:

$$\log\left(\frac{q_e}{q_e - q_t}\right) = \frac{k_1}{2.303} t \quad (2.3)$$

Then, rearrangement of Equation 2.4 at linear form:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2.4)$$

Where  $q_e$  (mg/g) is the amount of equilibrium uptake,  $q_t$  (mg/g) is the amount of solute adsorbed at any time  $t$ ,  $k_1$  is the rate constant of pseudo first order model ( $\text{min}^{-1}$ ) and is specified in Equation 2.5. If the experimental data can be fitted well with pseudo first order, graph plotted with  $\log(q_e - q_t)$  versus  $t$  is a straight line. Generally, when adsorption is initial by diffusion through a boundary, the kinetics will follow pseudo first order model in most cases (Crini et al., 2007).

$$q_t = \frac{(C_o - C_e)}{W} V \quad (2.5)$$

Where,  $C_e$  and  $C_o$  are the equilibrium and initial concentration of solutions (mg/L), separately.  $W$  (g) is the mass of the dry adsorbent used and  $V$  (L) is the volume of the solution.

### 2.5.1(b) Pseudo second order model

This model equation (Ho et al., 2000) based on equilibrium adsorption can be listed as Equation 2.6:

$$\frac{dq_t}{(q_e - q_t)} k_2 dt \quad (2.6)$$

Integrating equation 2.6 in condition  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$ , gives the integrated rate law for pseudo second order kinetic model:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \quad (2.7)$$

Equation 2.7, then rearranged to obtain a linear equation:

$$\frac{t}{q_t} = \frac{1}{q_e^2 k_2} + \frac{1}{q_e} t \quad (2.8)$$

The plot of  $\frac{t}{q_t}$  versus  $t$  gives a straight line with  $\frac{1}{q_e}$  and  $\frac{1}{q_e^2 k_2}$  as the slope and intercept if pseudo second order is applicable.  $K_2$  and  $q_e$  can be obtained directly from the graph without having to know the parameters previously. This kinetic model is more likely to apply onto the whole range of adsorption studies and it shows that chemisorption is the rate determining step (Ho et al., 2000; Crini et al., 2007).

### 2.5.1(c) Elovich's model

To further prove in term of chemisorption, the Elovich's model was applied. The Elovich model calculation is as displayed below (López et al., 2012):

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (2.9)$$

Where the underlying sorption amount (mg/g min) represent by  $\alpha$ ,  $\beta$  is identified with the expanded exterior exposure, and performing vitality for chemisorption (g/mg). Through linear plot  $q_t$  versus  $\ln t$ , estimation of  $\alpha$  and  $\beta$  can be acquired.

#### **2.5.1(d) Intra particle diffusion**

Internal or within particle diffusion has represented as rate of diffusion at early stage on adsorption. A straight line plot of  $q_t$  versus  $t^{0.5}$  that passes through origin was indicate the rate-controlling step. The Weber and Moris' model condition can be composed as (Weber & Morris, 1963):

$$q_t = Kt^{0.5} + c \quad (2.10)$$

Where, K is the intra particle diffusion rate constant (mg/g min) and c represent the intercept (mg/g).

#### **2.5.1(e) External diffusion**

The external or film diffusion model can be evaluated when zero intercept at origin in the graph of  $\ln (C_t/C_o)$  versus t. The equation of external diffusion has described as follows in Equation 2.11 (Anandkumar & Mandal, 2011):

$$\ln \frac{C_t}{C_o} = -k_{ext} t \quad (2.11)$$

Where  $C_t$  and  $C_o$  indicate the concentration of the solute in the liquid phase at time, t and initial solution and  $k_{ext}$  (1/min) is a diffusion rate parameter.

## 2.5.2 Adsorption isotherm

The equilibrium of the adsorption of sorbate on the surfaces of an adsorbent at a given pH and temperatures was described by using adsorption isotherm models. Plotting of the compound concentration stability in the adsorbent as a function of its equilibrium concentration solution was described as an isotherm study. (Delle Site, 2001).  $R^2$  value which is adjoining to unity demonstrates that the isotherm model contributes the perfect fit to the investigational data.

The isotherm adsorption model was used to describe how sorbates interact with the adsorbent by optimizing the use of the adsorbent. In this study, Langmuir, Freundlich, Dubinin-Radushkevich, Temkin and Halsey models have been studied.

### 2.5.2(a) Langmuir's model

The contaminations sorption lead to the Langmuir that has been taken into consideration. It depends on the suspicion concerning the monolayer adsorptions on a homogenous surface with uniform energies of adsorption for all the binding sites. In addition, no more adsorption process would happen if the site is possessed by a solute (Hall et al., 1966). The Langmuir isotherm equation in linear form can be signified by the following equation (Shrivastava & Gupta, 2011):

$$\frac{1}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (2.12)$$

Where  $C_e$  (mg/L) is the equilibrium concentration of the adsorbate,  $C_o$  (mg/L) is the underlying adsorbate concentration,  $q_e$  (mg/g) is the adsorption capacity at equilibrium,  $q_m$  (mg/g) and  $b$  (L/mg) are Langmuir consistent identified with the adsorption limit and the rate of adsorption, separately. In order to determine if the

adsorption process is favourable or unfavourable, dimensionless separation factor ( $R_L$ ) is calculated using the following equation (Hall et al., 1966).

$$R_L = \frac{1}{1 + bC_0} \quad (2.13)$$

A value of  $0 < R_L < 1$  shows unfavourable adsorption conditions;

$R_L < 1$  shows unfavourable adsorption conditions;

$R_L = 1$  shows linear adsorption conditions; and

$R_L = 0$  shows irreversible adsorption conditions.

### 2.5.2(b) Freundlich's model

Freundlich model is an empirical equation that assumes heterogeneous adsorption due to the diversity of adsorption active sites (Mckay et al., 1982). The Freundlich consistent gain from a plot of  $\log q_e$  versus  $\log C_e$ . The Freundlich linear type isotherm is as demonstrated as follows:

$$\log q_e = \log K_F + \frac{1}{n_F} \log C_e \quad (2.14)$$

Where  $K_F$  ( $(\text{mg/g}) (\text{L/mg})^{1/n}$ ) is the adsorption capacity, while Freundlich constants characterises by  $n$ , separately. Larger value of  $K_F$  point to greater adsorption capacity, while  $n_F$  values designate the prefer ability of the adsorption process (Tseng & Wu, 2008). The adsorption process is favourable for physical adsorption if  $n_F$  is above unity. The further details of  $n_F$  values can be used to anticipate the adsorption consumption in a calculated adsorption system as shown in **Table 2.4**.

**Table 2.4:** Relationship between  $n_F$  value in Freundlich's equation, isotherm curve type and its favourable level (Tseng & Wu, 2008)

$n_F$	Isotherm curve type	Favourable level
$n_F > 100$	Pseudo-rectangular	Pseudo-irreversible
$100 > n_F > 10$	Hastily rise	Strong favourable
$10 > n_F > 2$	Mildly rise	Favourable
$2 > n_F > 1$	Pseudo-linear	Pseudo-linear
$n_F = 1$	Linear	Linear
$n_F < 1$	Concave up	Unfavourable

### 2.5.2(c) Dubinin-Radusckich's model

The D-R isotherm study has been generally employed in order to determine the high degree of rectangularity (Dubinin & Radushkevich, 1947). The D-R isotherm equation in the linear form displayed below:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (2.15)$$

Where  $\beta$  ( $\text{mol}^2/\text{kJ}^2$ ) signifies the constant of an adsorption constant acquired from the slope of the linear plot of  $\ln q_e$  versus  $\varepsilon^2$  and  $\varepsilon$ , the Polanyi potential, can be intended by the subsequent equation:

$$\varepsilon = RT \ln[1 + 1/C_e] \quad (2.16)$$

Where T is the temperature in Kelvin (K) and R is the universal gas constant in  $\text{kJ}/(\text{mol K})$ . The mean free energy, E ( $\text{kJ}/\text{mol}$ ) can be calculated by the displayed equation:

$$E = 2\beta^{-0.5} \quad (2.17)$$

### 2.5.2(d) Temkin's model

In addition, other model for the study of indirect adsorbent/adsorbate relations on adsorption is Temkin model (Temkin & Pyzhev, 1940). This isotherm deduced that

the heat of adsorption all the molecules in the layer would linearly decline with coverage and the adsorption is categorised by binding energies in a uniform distribution, catching up to maximum binding energy. The linear form of Temkin isotherm equation is as follows:

$$q_e = \ln K_T + \beta \ln C_e \quad (2.18)$$

Where  $\beta = RT/b_T$ . A plot of  $q_e$  versus  $\ln C_e$ , constant  $K_T$  and  $b_T$  can be instigated from the intercept and slope. The  $b_T$  (J/mol) is Temkin constant related to the heat of adsorption, while  $K_T$  (L/mg) represents Temkin constant associated to the equilibrium binding energy.

### 2.5.2(e) Halsey's model

The Halsey adsorption isotherm is suitable for multilayer adsorption and the fitting of the experimental data to this equation demonstrate the heterogenous nature of the adsorbent. This model commonly represented as equation 2.19:

$$\ln q_e = \left[ \frac{1}{n} \ln K_H \right] - \frac{1}{n} \ln C_e \quad (2.19)$$

Where  $K_H$  and  $n$  are the Halsey isotherm constant and exponent, respectively. The linear plot of  $\ln q_e$  versus  $\ln C_e$  of Halsey's model indicate the heteroporosity (macropore and mesopore) of the adsorbents.