SYNTHESIS OF CARBON NANOTUBES - MESOSTRUCTURED SILICA NANOPARTICLES COMPOSITES FOR ADSORPTION OF METHYLENE BLUE

AINUL HAKIMAH KARIM

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Doctor of Philosophy (Chemistry)

Faculty of Science
Universiti Teknologi Malaysia

FEBRUARY 2015

ABSTRACT

The mesostructured silica nanoparticles (MSN) have been widely developed for the removal of various pollutants due to their highly porous structure and other novel features. While carbon nanotubes (CNT) are attracting great interest owing to its large specific surface area, small size, hollow and layered structures. The integration of these outstanding properties by modification of MSN with singlewalled CNT (SWCNT) and multiwalled CNT (MWCNT) is quite new in this area of study and is expected to produce an adsorbent with higher adsorption capacity. In this study, three types of adsorbents were prepared by a simple one step method; MSN, series of SWCNT-MSN composites, and series of MWCNT-MSN composites. Their characteristics have been observed by XRD, N_2 physisorption, FTIR, TEM, and FESEM, while their adsorption performance were evaluated on the adsorption of methylene blue (MB) at various pH, adsorbent dosage, initial MB concentration, and temperature. The results demonstrated that the adsorbents were prepared with mesoporous structures and produces relatively higher number of pores with larger diameters. The CNTs were found to improve the physicochemical properties of the MSN and led to an enhanced adsorptivity for MB. N_2 physisorption measurements revealed the development of a bimodal pore structure in MWCNT-MSN composites that increased the pore size, pore volume and surface area. The best conditions for MSN, SWCNT-MSN and MWCNT-MSN composites achieved at pH 7 and 303 K using 0.05 g L^{-1} adsorbent and 100 mg L^{-1} MB. Fitting with linear Langmuir isotherm produce the maximum adsorption capacity of 500.1 mg g^{-1}, 500.0 mg g^{-1}, and 263.2 mg g^{-1} for MSN_{AP}, SWCNT-MSN and MWCNT-MSN, respectively. The equilibrium data were evaluated using the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isotherm models, with the Freundlich model affording the best fit to the adsorption data for MSN and Langmuir model for both SWCNT-MSN and MWCNT-MSN. The adsorption kinetics for all MSN, SWCNT-MSN and MWCNT-MSN were best described by the pseudo-second order model. Thermodynamic study showed that the nature of MSNs and MWCNT-MSNs are exothermic, and endothermic for SWCNT-MSNs. This study is proven to produce a relatively new and potential mesostructured materials used as adsorbent for dye removal and water treatment.

ABSTRAK

Zarahnano silika mesoliang (MSN) telah dikaji dengan meluas untuk tujuan merawat pelbagai jenis bahan cemar berdasarkan ketinggian struktur berliangnya dan ciri-ciri istimewa lain yang dimilikinya. Manakala karbon bertiub-nano (CNT) telah menarik perhatian ramai penyelidik kerana luas permukaan yang tinggi, saiz yang kecil, serta struktur yang berongga dan berlapis. Integrasi sifat-sifat pada dua bahan ini menerusi modifikasi antara MSN, dan dua jenis CNT iaitu CNT dinding tunggal (SWCNT) dan CNT multi-dinding (MWCNT) merupakan kajian yang baru dalam bidang ini dan dijangka menghasilkan penjerap dengan keupayaan penjerapan yang tinggi. Dalam kajian ini, tiga jenis penjerap telah disintesis menggunakan satu kaedah yang ringkas; iaitu MSN, siri komposit SWCNT-MSN, dan siri komposit MWCNT-MSN. Sifat-sifat penjerap telah dicirikan menggunakan XRD, N_2 physisorption, FTIR, TEM dan FESEM, manakala prestasi penjerapan mereka telah dinilai keatas metilena biru (MB) pada pelbagai pH, dos penjerap, kepekatan MB awal, dan suhu. Keputusan menunjukkan penjerap memiliki struktur berliang dan bilangan liang yang tinggi dengan diameter yang besar. CNT dipercayai telah meningkatkan sifat kimia-fizik MSN seterusnya menggalakkan penjerapan terhadap MB. Pengukuran dengan N_2 mendedahkan penghasilan struktur liang bimodal dalam komposit MWCNT-MSN yang menambah saiz dan isipadu liang, serta luas permukaan. Keadaan terbaik untuk ketiga-tiga jenis penjerap MSN, SWCNT-MSN dan MWCNT-MSN telah dicapai pada pH 7, bersuhu 303 K menggunakan 0.05 g L^{-1} penjerap dan kepekatan awal MB 100 mg L^{-1}. Keupayaan penjerapan maksimum Langmuir untuk MSN_{AP}, MWCNT-MSN dan SWCNT-MSN masing-masing adalah 500.1 mg g^{-1}, 500 mg g^{-1}, dan 263.2 mg g^{-1}. Data keseimbangan telah ditaksir dengan model isotherm Langmuir, Freundlich, Temkin, dan Dubinin-Radushkevich, dengan model Freundlich paling sesuai untuk MSN dan model Langmuir paling sesuai untuk MWCNT-MSN dan SWCNT-MSN. Kinetik penjerapan untuk kesemua penjerap MSN, SWCNT-MSN dan MWCNT-MSN pula menepati model tertib pseudo-kedua. Kajian termodinamik menunjukkan MSN dan MWCNT-MSN bersifat eksotermik, manakala SWCNT-MSN bersifat endotermik. Dapatan kajian ini membuktikan bahan berstruktur mesoliang yang baru dan berpotensi telah berjaya disediakan dan digunakan sebagai penjerap dalam penyingkiran pewarna dan rawatan air.

TABLE OF CONTENT

CHAPTER	TITLE	PAGE
	TITLE	i
	DECLARATION	ii
	ABSTRACT	iii
	ABSTRAK	iv
	TABLE OF CONTENTS	v
	LIST OF TABLES	viii
	LIST OF FIGURES	ix
	LIST OF ABBREVIATIONS	xii
	LIST OF SYMBOLS	xiii
	LIST OF APPENDICES	xiv
1	**INTRODUCTION**	**1**
	1.1 Research Background	1
	1.2 Problem Statement and Hypothesis	4
	1.3 Objectives of Study	5
	1.4 Scopes of Study	5
	1.5 Significance of Study	6
	1.6 Thesis Outline	7
2	**LITERATURE REVIEW**	**9**
	2.1 Dye Removal	9
	2.1.1 Methylene Blue	12
	2.1.2 Adsorption of Methylene Blue	14
	2.2 Adsorption Study	15
	2.2.1 Equilibrium Isotherm Model	16

		2.2.2 Kinetic Study	20
		2.2.3 Thermodynamics Study	21
	2.3	Mesostructured Silica Nanoparticles	22
		2.3.1 Synthesis of Mesostructured Silica	23
		2.3.2 Modification of Mesostructured Silica Nanoparticles	26
		2.3.3 Characterization of Mesostructured Silica	28
		2.3.3.1 Powder X-ray Diffraction	29
		2.3.3.2 Nitrogen Sorption Analysis	29
		2.3.3.3 Scanning and Transmission Electron Microscopy	31
		2.3.4 Adsorption of Methylene Blue onto Mesostructured Silica	32
	2.4	Carbon Nanotubes	34
		2.4.1 Modification of Carbon Nanotubes	36
		2.4.2 Adsorption of Methylene Blue onto Carbon Nanotubes	37
	2.5	Carbon Nanotubes – Silica Composite	40
	2.6	Summary	42
3		**METHODOLOGY**	**43**
	3.1	Preface	43
	3.2	Materials and Chemicals	44
	3.3	Syntheses of Adsorbents	44
		3.3.1 Synthesis of MSN	44
		3.3.2 Synthesis of CNT-MSN	45
	3.4	Characterization of Adsorbents	46
		3.4.1 XRD	46
		3.4.2 Morphological Analysis	47
		3.4.3 Nitrogen Physisorption	47
		3.4.4 FTIR	48
	3.5	Adsorption of MB onto Adsorbents	49
	3.6	Analysis of Adsorption	50

	3.6.1 Equilibrium Isotherm	51
	3.6.2 Kinetics Study	51
	3.6.3 Thermodynamics Study	51
4	**RESULTS AND DISCUSSION**	**53**
	4.1 Preface	53
	4.2 Syntheses of Adsorbents	53
	4.3 Characterization of Adsorbents	54
	4.3.1 XRD Analysis	54
	4.3.2 Nitrogen Physisorption Analysis	57
	4.3.3 FTIR Analysis	62
	4.3.4 Morphological Analysis	67
	4.3.5 Proposed Mechanism of Synthesis of CNT-MSN composites	70
	4.4 Adsorption Studies	72
	4.4.1 Performance of MSN and CNT-MSN towards MB Adsorption	72
	4.4.2 Effect of pH	73
	4.4.3 Effect of Adsorbent Dosage	75
	4.4.4 Equilibrium Isotherm Studies	77
	4.4.5 Kinetics Studies	85
	4.4.6 Thermodynamics Studies	90
	4.5 Regeneration of Adsorbents	95
	4.6 Summary	96
5	**CONCLUSION**	**97**
	5.1 Summary	97
	5.2 Future Work	98
REFERENCES		**99-116**
Appendices A - E		117-124

LIST OF TABLES

TABLE NO.	TITLE	PAGES
2.1	Summary of treatment technologies to remove dyes	10
2.2	Effect of methylene blue	13
2.3	Adsorption of Methylene Blue onto various adsorbents	14
2.4	Summary of equilibrium isotherms	19
2.5	Main parameters in the synthesis of mesostructured silica (Meynen *et al*., 2009)	23
2.6	Adsorption of Methylene Blue onto Mesostructured Silica	34
2.7	Maximum Adsorption Capacity of MB on CNT and CNT composites	39
3.1	Description of adsorbents	46
4.1	Textural properties of MSNs and CNT-MSNs composites	61
4.2	FTIR band assignments	64
4.3	Isotherm parameters for MB adsorption onto MSN and CNT-MSN composites	84
4.4	Kinetics parameters for MB adsorption onto MSN and CNT-MSN composites	89
4.5	Thermodynamic parameters for the adsorption of MB onto MSN and CNT-MSN composites at different temperatures	94
4.6	Comparison of the adsorption of Methylene Blue	96

LIST OF FIGURES

FIGURE NO.	TITLE	PAGES
2.1	Structure of Methylene Blue	13
2.2	Honeycomb structure of MCM-41 observed by Transmission Electron Microscopy (Meynen *et al.*, 2009)	25
2.3	Curved nature of the pore of SBA-15 observed by Transmission Electron Microscopy (Meynen *et al.*, 2009)	26
2.4	Organic modification of mesostructured silica by grafting at terminal organosilanes (Hoffmann *et al.*, 2006)	27
2.5	Organic modification of mesostructured silica by co-condensation method (Hoffmann *et al.*, 2006)	27
3.1	Research Flow	43
4.1	XRD pattern of MSN_{UN} and MSN_{AP}	54
4.2	XRD pattern of SWCNT-MSN composites	55
4.3	XRD pattern of MWCNT-MSN composites	56
4.4	Nitrogen adsorption-desorption isotherms (A) and pore size distribution (B) of MSN_{UN} and MSN_{AP}	57
4.5	Nitrogen adsorption-desorption isotherms (A) and pore size distribution (B) of SWCNT-MSN composites	59
4.6	Nitrogen adsorption-desorption isotherms (A) and pore size distribution (B) of MWCNT-MSN composites	60
4.7	FTIR Spectra of MSN_{UN}, MSN_{AP} and MSN_{AP} - MB	62
4.8	FTIR Spectra of MB	63
4.9	FTIR Spectra of SWCNT-MSN composites	65

4.10	FTIR Spectra of MWCNT-MSN composites	65
4.11	FESEM (A) and TEM images (B) of MSN_{AP}	67
4.12	FESEM (A) and TEM images (B) of SWCNT-MSN composites	68
4.13	FESEM (A) and TEM images (B) of MWCNT-MSN composites	69
4.14	Schematic diagram of synthesized SWCNT-MSN composites	70
4.15	Schematic diagram of synthesized MWCNT-MSN composites	70
4.16	Schematic Diagram for the adsorption process of the surfactant on the CNT-aqueous interfaces	71
4.17	Performance of adsorbents towards the adsorption of MB	73
4.18	Effect of pH on adsorption of MB on MSN_{UN} and MSN_{AP} (A), SWCNT-MSN (B) and MWCNT-MSN (C)	74
4.19	Isoelectric point (pH_{zpc}) of MWCNT-MSN composites	75
4.20	Effect of MSN_{AP} (A), SWCNT-MSN (B) and MWCNT-MSN (C) dosage on the adsorption of MB	76
4.21	Linear plots of isotherm models for adsorption of MB onto MSN_{AP} (adsorbent dosage 0.1 g L^{-1}, initial pH 7, 25°C) (A) Langmuir, (B) Freundlich, (C) Temkin, and (D) Dubinin-Radushkevich	78
4.22	Linear plots of isotherm models for adsorption of MB onto SWCNT-MSN composites (adsorbent dosage 0.1 g L^{-1}, initial pH 7, 25°C) (A) Langmuir, (B) Freundlich, (C) Temkin, and (D) Dubinin – Radushkevich	79
4.23	Linear plots of isotherm models for adsorption of MB onto MWCNT-MSN composites (adsorbent dosage 0.1 g L^{-1}, initial pH 7, 25°C) (A) Langmuir, (B) Freundlich, (C) Temkin, and (D) Dubinin – Radushkevich	80

4.24	Pseudo-second order kinetics model plot for adsorption of MB onto MSN_{AP} (A), and Weber-Morris intraparticle diffusion plot (B)	86
4.25	Pseudo-second order kinetics model plot for adsorption of MB onto SWCNT-MSN composites (A), and Weber-Morris intraparticle diffusion plot (B)	87
4.26	Pseudo-second order kinetics model plot for adsorption of MB onto MWCNT–MSN composites (A), and Weber-Morris intraparticle diffusion plot (B)	87
4.27	Plot of ln K_c versus *1/T* for estimation of thermodynamic parameters for the adsorption of MB onto MSN_{AP} (A), SWCNT-MSN (B) and MWCNT-MSN (C)	91
4.28	Regeneration of MSN, SWCNT-MSN, and MWCNT-MSN adsorbents on adsorption of MB [C_o=100 mg g^{-1}, pH 7, t=2h, 303 K]	95

LIST OF ABBREVIATIONS

APTES	-	3-aminopropyl triethoxysilane
BET	-	Brunauer Emmet Teller
BJH	-	Barrett, Joyner, and Halenda
CNT	-	Carbon Nanotubes
CTAB	-	Cetyl Trimethyl Ammonium Bromide
FESEM	-	Field Emission Scanning Electron Field
FTIR	-	Fourier Transform Infra-Red
MB	-	Methylene Blue
MCM-41	-	Mobil Compound Mesoporous – 41
MSN	-	Mesostructured Silica Nanoparticles
MSN_{AP}	-	Mesostructured Silica Nanoparticles prepared with APTES
MSN_{UN}	-	Mesostructured Silica Nanoparticles prepared without APTES
MWCNT	-	Multiwalled CNT
SBA-15	-	Santa Barbara Amorphous -15
SWCNT	-	Singlewalled CNT
TEM	-	Transmission Electron Field
TEOS	-	Tetra Ethyl Ortho Silicate
XRD	-	X-Ray Diffraction

LIST OF SYMBOLS

C_i	-	Thickness of the boundary layer
C_o	-	Initial MB concentration (mg L^{-1})
C_t	-	MB concentration at time t of reaction (mg L^{-1})
C_e	-	MB concentration at equilibrium time (mg L^{-1})
k_1	-	Pseudo-first order rate constant (min^{-1})
k_2	-	Pseudo-second order rate constant (mg g^{-1} min^{-1})
k_{id}	-	intraparticle diffusion constant (mg g^{-1} $min^{-1/2}$)
K	-	Kelvin
K_L	-	Langmuir constant
K_F	-	Freundlich constant
K_T	-	Temkin constant
K_{DR}	-	Dubunin-Radushkevich constant
m	-	Mass (g)
n_F	-	Heterogenity factor
q_e	-	Adsorption uptake at equilibrium conditions (mg g^{-1})
q_t	-	Adsorption uptake at time t (mg g^{-1})
q_m	-	Maximum adsorption capacity (mg g^{-1})
R	-	Gas constant (8.314 J mol^{-1} K^{-1})
T	-	Absolute temperature (K)
V	-	Volume of solution (L)

LIST OF APPENDICES

APPENDIX	TITLE	PAGES
A	Raw XRD Pattern	117
B	Calculation of Adsorption Capacity	118
C	Pseudo-first order kinetics model plot for adsorption of MB onto MSN_{AP}	120
D	Pseudo-first order kinetics model plot for adsorption of MB onto SWCNT-MSN	121
E	Pseudo-first order kinetics model plot for adsorption of MB onto MWCNT-MSN	122
F	List of Publications / Proceedings	123

CHAPTER 1

INTRODUCTION

1.1 Research Background

The increasing development of wide range of industries was resulted to the discharge of highly coloured and variety of synthetic dye effluents into water stream. Moreover, the large-scale production of synthetic dyes which are potentially toxic to living organisms and even carcinogenic to humans and aquatic life is of great environmental concerns (NIOSH, 1980; Moreira, 2004).

In order to solve this environmental issue, various treatment methods have been studied, developed, and reviewed to remove dyes and other pollutants from wastewater. Some of them are flocculation, sedimentations, flotation, filtration, membrane separations, ion-exchange, oxidation and adsorption. Among them, adsorption process has been established as an effective and simple approach to remove dye from wastewater. For this purpose, activated carbons have become one of the most widely used adsorbents. However, these materials suffer from some drawbacks, such as costly regenerations, non-selective uptake as well as the adsorption capacity requires other types of materials to be proposed, developed and evaluated to meet this need (Walcarius and Mercier, 2010).

With increasing environmental concerns worldwide, nanoporous materials have given attention for the separation of polluting species and the recovery of useful ones. Environmentally and friendly zeolites were studied extensively. The reason for their success is related to their specific features in converting molecules having kinetic diameter below 1 nm, but they become insufficient when reactants with sizes larger than the pores is targeted. Research efforts to synthesize materials with larger pore diameter, high structural stability and adsorptive activity in extending the applications of zeolites come with a new material namely mesoporous or mesostructured silica nanoparticles.

Mesostructured silica nanoparticles have been well developed in these two decades since the discovery by Mobil researchers (Kresge *et al.*, 1992), Kuroda and his co-workers (Yanagisawa *et al.*, 1990), and (Inagaki *et al.*, 1993). This material, with large pore diameters ranging from 2 to 50 nm have been a focus of many researches because of their high specific surface areas, controllable structures and compositions, which make them suitable for a wide range of applications in catalysis, adsorption, separation, chromatography, etc. The pore size of mesoporous silica is large enough to accommodate a variety of large and bulky molecules, and the high density of silanol groups on the pore wall is beneficial to the introduction of functional groups with a high coverage.

Various kinds of surface modifications have been conducted for providing new functions for the surfaces of mesostructured in order of making them suitable for a wide range of applications such as in catalysis, adsorption, separation, and chromatography.

Carbon nanotubes (CNTs) have attracted great attention in nanoscale science and technology due to their unique optical, electronic and mechanical properties (Popov, 2004; Smart *et al.*, 2006; Wu *et al.*, 2009; Eder, 2010). They are an attractive alternative for the removal of organic and inorganic contaminants from water, because they have a large specific surface area, small size, hollow and layered structures. Furthermore, the wide range of unique features of CNTs specifically in their adsorption properties are resulted from their hollow, layered nanosized structures (Rodríguez *et al.*, 2010; Yao *et al.*, 2010b), and strong van der Waals binding energy for molecular adsorbates on adsorption sites (Ren *et al.*, 2011). Recently, CNTs have been found to be efficient adsorbents with a capacity that exceeds that of activated carbon (Long and Yang, 2001; Lu and Chiu, 2006).

However, the formation of CNT aggregates limits the ability of CNTs to disperse homogeneously in various solvents and also causes difficulties in the separation process (Wang *et al.*, 2010). Considering the potential use of CNTs in wastewater treatment, numerous studies have been done on their hybridization with other materials such as chitosan (Chatterjee *et al.*, 2010), activated carbon fiber (Wang *et al.*, 2010), graphene (Ai and Jiang, 2012), and cellulose (Deng *et al.*, 2012) in order to enhance their dispersion properties and adsorption capacities.

Several efforts have been also made to hybridize CNTs with other well-performing materials. For instance, alumina coated onto CNT improved their ability to remove Pb(II) and Ni(II) ions (Amais *et al.*, 2007) as compared to the parent, while mesoporous TiO_2-CNT composites improved the photodegradation of the air pollutant acetone (Yu *et al.*, 2005). In addition, CNTs have also been hybridized with mesoporous silica materials such as SBA-15 (Vila *et al.*, 2009) and MCM-41 (Wang *et al.*, 2009) in which the physical properties of the composites were reported have been improved.

However, as the best to our knowledge, detailed studies on the effect of modification with CNTs upon the physicochemical properties of mesostructured silica nanoparticles (MSN) as well as their subsequent application to dye adsorption is still rare. Therefore, in this study we report on a preparation of MSN loaded with different percentages of multiwalled CNTs (MWCNT) and singlewalled CNT (SWCNT) to produce a series of CNT-MSN composites. The synthesized CNT-MSN composites were then characterized by X-ray diffraction, Fourier transform infrared spectroscopy, nitrogen physisorption, and transmission electron microscopy. We found that the physicochemical properties of the composite were improved in term of the interaction between adsorbents, and thus enhanced their adsorption capability towards MB dye. The adsorption equilibrium, kinetics and thermodynamics of the adsorption were also investigated.

1.2 Problem Statement and Hypothesis

Discharge of methylene blue dye effluents from industrial area into water stream may cause serious environmental effects especially to aquatic life and their consumers, due to their toxicity, harmful, and carcinogenic effect. Moreover, solubility and stability of methylene blue in water made this kind of dye difficult to be removed by conventional methods. Therefore, finding and developing the most practical method and material for this purpose is beneficial.

To date, adsorption has been established for the simple, easy and effective approach in removal technology. For this purpose, activated carbons have become one of the most widely used adsorbents. However, these materials suffer from some disadvantages, such as costly regenerations, non-selective uptake. Hence, the adsorption capacity requires other types of materials to be proposed, developed and evaluated to overcome these disadvantages (Gong *et al.*, 2009; Walcarius and Mercier, 2010; Ren *et al.*, 2011).

Mesostructured silica nanoparticles adsorbent with outstanding features has been explored for the removal of various pollutants (Walcarius and Mercier, 2010). This material becomes great interest due to their high specific surface area, high thermal and mechanical stability, and highly uniform pore distribution. These outstanding features make it an excellent adsorbent with high adsorption capacity. However, adsorption of methylene blue needs adsorbent with ultimately high surface area and high interaction in such way to improve the efficiency of adsorption. Therefore, modification of MSN with carbon nanotubes (CNTs) was studied.

Carbon nanotubes (CNTs) have attracted great attention in nanoscale science and technology due to their unique optical, electronic and mechanical properties, also good adsorption capacities due to their hollow, layered nanosized structures. However, the formation of CNT aggregates limits the ability of CNTs to disperse homogeneously in various solvents and also causes difficulties in the separation process

The modification of MSN with carbon nanotubes (CNT-MSN) was quite new in this area of study. They have not been explored extensively to remove dye via adsorption. It is expected to enhance adsorption activity in term of the adsorption capacity, rate of adsorption, and its selectivity towards wide range of pollutants. The integration of the superior feature of mesostructured silica nanoparticles and carbon nanotubes were estimated to generate a competent material as adsorbents. The combination structure of both materials is expected to improve the physical properties of CNT or MSN alone (high surface area and pore amount) and subsequently may increase the physical interaction which may led to high adsorption capacity towards methylene blue dye. Besides, the structure of CNT with high π-π interaction may attract the MB molecules at the benzene ring structure (Li *et al.*, 2014).

1.3 Objectives of Study

The objectives of this study are:

1. To synthesize mesostructured silica nanoparticles (MSN) and modified MSN with carbon nanotubes (CNT-MSN) adsorbent.
2. To characterize MSN and CNT-MSN adsorbents.
3. To determine the performance of adsorbents towards the adsorption of methylene blue.
4. To determine the equilibrium isotherm, kinetics, and thermodynamics of MSN and CNT-MSN adsorbents.

1.4 Scope of Study

This study comprises some components in order to complete the objectives outlined in this study. Typically, mesostructured silica nanoparticles (MSN) were synthesized from cetyltrimethylammonium bromide (CTAB) as structure-directing agent or template, TEOS as silica source and ammonia solution by sol-gel method. The synthesis takes place at 323 K. Next, the obtained sol-gel was aged, centrifuged, washed, dried and calcined at 823 K.

A part of this study involves synthesis of MSN with an addition of 3-aminopropyl triethoxysilane (APTES) as pore expander. The APTES was introduced to the MSN by co-condensation method. Another part of this study is modification of MSN with CNT. Two types of CNT was used, they are MWCNT and SWCNT.

The prepared MSNs and CNT-MSNs composites were characterized by XRD, N_2 physisorption, FTIR, TEM, and FESEM to establish their physicochemical-properties in term of mesostructured phase and crystallinity, surface area, pore size distribution, and particle size.

Next, the performances of the adsorbents were executed towards the adsorption of methylene blue in aqueous solution. The adsorption process is carried out in a batch system under varying pH (2-11), adsorbent dosage (0.1-0.5 g L^{-1}), initial MB concentration (5-100 mg L^{-1}), and temperature (303-323 K).

The adsorption mechanism of MB onto adsorbents was studied over equilibrium isotherm, kinetics models and thermodynamic. The four widely used isotherm model were used to study the adsorption behavior, they are Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich. Meanwhile, three conventional kinetic models, namely Lagergren pseudo-first order, Ho pseudo-second order, and Weber and Morris Intraparticle diffusion model have been used. Lastly, the adsorption enthalpy ($\Delta H°$), entropy ($\Delta S°$) and Gibbs free energy ($\Delta G°$) were calculated using the thermodynamic functions.

1.5 Significance of Study

This study was accomplished to prepare mesostructured silica and CNT-MSN composites. The prepared materials were characterized and the adsorptive ability of the prepared material was studied in details to elucidate the relationship of their physicochemical properties with the performance. The prepared CNT-MSN with larger pore size improved the adsorptive sites and further enhances the adsorption of MB dye which is beneficial for water treatment technologies. Hence, this study is looking forward to contribute for the knowledge in mesostructured silica researches.

1.6 Thesis Outline

This proposal reported the synthesis of mesostructured silica nanoparticles and its modification with CNT, which then studied towards methylene blue adsorption from aqueous solution. This proposal was divided into five chapters. Chapter 1 introduces the background of the research, problem statement and hypothesis, objectives of study, scopes of study, its significance, and lastly thesis outline for this study.

In chapter 2, the literature related to this study was reviewed. They consist of an overview of the mesostructured silica and carbon nanotubes material since they were discovered and their special features to be developed as potential adsorbents. Then, the vicinity of adsorption study was elaborated to obtain a deep understanding, such as equilibrium study, kinetics, and thermodynamics.

Chapter 3 explains the research design and methodology utilized in order to complete this work. This chapter describes the material used, experimental procedure, characterization methods, and adsorption study of adsorbents.

Chapter 4 discusses the experimental results performed in this study. First part explains the physicochemical properties of all synthesized adsorbents by XRD, N_2 physisorption, FTIR, TEM, and FESEM. Next, their performances towards adsorption of methylene blue were observed. In this section, the effect of pH, adsorbents dosage, initial concentration of methylene blue solution, and temperature was studied, in line with the equilibrium isotherm, kinetic and thermodynamic view of the adsorption.

Chapter 5 describes the summary derived from these study and listed the future work to be executed in order to expand this potential materials and further contribute to the knowledge.

REFERENCES

Abidin, M. A. Z., Jalil, A. A., Triwahyono, S., Adam, S. H. and Kamarudin, N. H. N. (2011). Recovery of gold(III) from an aqueous solution onto a durio zibethinus husk. *Biochemical Engineering Journal* 54 (2), 124-131.

Abramian, L. and El-Rassy, H. (2009). Adsorption kinetics and thermodynamics of azo-dye Orange II onto highly porous titania aerogel. *Chemical Engineering Journal* 150, 403-410.

Agnihotri, S., Mota, J. P. B., Rostam-Abadi, M. and Rood, M. J. (2005). Structural Characterization of Single-Walled Carbon Nanotube Bundles by Experiment and Molecular Simulation. *Langmuir* 21 (3), 896-904.

Agnihotri, S., Mota, J. P. B., Rostam-Abadi, M. and Rood, M. J. (2006). Theoretical and experimental investigation of morphology and temperature effects on adsorption of organic vapors in single-walled carbon nanotubes *Journal of Physical Chemistry B* 110, 7640-7647.

Aharoni, C. and Ungarish, M. (1977). Kinetics of activated chemisorption. Part 2.-Theoretical models. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases* 73 (0), 456-464.

Ahmad, A. A., Hameed, B. H. and Aziz, N. (2007). Adsorption of direct dye on palm ash: Kinetic and equilibrium modeling. *Journal of Hazardous Materials* 141 (1), 70-76.

Ai, L. and Jiang, J. (2012). Removal of methylene blue from aqueous solution with self-assembled cylindrical graphene–carbon nanotube hybrid. *Chemical Engineering Journal* 192 (0), 156-163.

Ai, L., Zhang, C., Liao, F., Wang, Y., Li, M., Meng, L. and Jiang, J. (2011). Removal of methylene blue from aqueous solution with magnetite loaded multi-wall carbon nanotube: Kinetic, isotherm and mechanism analysis. *Journal of Hazardous Materials* 198 (0), 282-290.

Al-Futaisi, A., Jamrah, A. and Al-Hanai, R. (2007). Aspects of cationic dye molecule adsorption to palygorskite. *Desalination* 214 (1), 327-342.

Amais, R. S., Ribeiro, J. S., Segatelli, M. G., Yoshida, I. V. P., Luccas, P. O. and Tarley, C. R. T. (2007). Assessment of nanocomposite alumina supported on multi-wall carbon nanotubes as sorbent for on-line nickel preconcentration in water samples. *Separation and Purification Technology* 58 (1), 122-128.

Anbia, M. and Hariri, S. A. (2010). Removal of methylene blue from aqueous solution using nanoporous SBA-3. *Desalination* 261 (1–2), 61-66.

Anbia, M. and Lashgari, M. (2009). Synthesis of amino-modified ordered mesoporous silica as a new nano sorbent for the removal of chlorophenols from aqueous media. *Chemical Engineering Journal* 150, 555-560.

Anbia, M. and Salehi, S. (2012). Removal of acid dyes from aqueous media by adsorption onto amino-functionalized nanoporous silica SBA-3. *Dyes and Pigments* 94 (1), 1-9.

Annadurai, G., Juang, R.-S. and Lee, D.-J. (2002). Use of cellulose-based wastes for adsorption of dyes from aqueous solutions. *Journal of Hazardous Materials* 92 (3), 263-274.

Araujo, R. S., Azevedo, D. C. S., Jr., C. L. C., Jimenez-Lopez, A. and Rodrıguez-Castellon, E. (2008). Adsorption of polycyclic aromatic hydrocarbons (PAHs) from isooctane solutions by mesoporous molecular sieves: Influence of the surface acidity. *Microporous and Mesoporous Materials* 108, 213-222.

Atar, N. and Olgun, A. (2007). Removal of acid blue 062 on aqueous solution using calcinated colimanite ore waste. *Journal of Hazardous Materials* 146, 171-179.

Atkin, R., Craig, V. S. J., Wanless, E. J. and Biggs, S. (2003). Mechanism of cationic surfactant adsorption at the solid–aqueous interface. *Advances in Colloid and Interface Science* 103 (3), 219-304.

Bailey, S. E., Olin, T. J., Bricka, R. M. and Adrian, D. D. (1999). A review of potentially low-cost sorbents for heavy metals. *Water Research* 33 (11), 2469-2479.

Barrett, E. P., Joyner, L. G. and Halenda, P. P. (1951). The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms. *Journal of the American Chemical Society* 73, 373–380.

Beck, J. S., Vartuli, J. C., Roth, W. J., Leonowicz, M. E., Kresge, C. T., Schmitt, K. D., Chu, C. T. W., Olson, D. H. and Sheppard, E. W. (1992). A new family of mesoporous molecular sieves prepared with liquid crystal templates. *Journal of the American Chemical Society* 114 (27), 10834-10843.

Bestani, B., Benderdouche, N., Benstaali, B., Belhakem, M. and Addou, A. (2008). Methylene blue and iodine adsorption onto an activated desert plant. *Bioresource Technology* 99 (17), 8441-8444.

Bhattacharyya, K. G. and Sharma, A. (2005). Kinetics and thermodynamics of Methylene Blue adsorption on Neem (Azadirachta indica) leaf powder. *Dyes Pigments* 65, 51-59.

Blass, N. and Fung, D. (1976). Dyed but not dead-methylene blue overdose. *Anesthesiology* 45, 458-459.

Brunauer, S., Emmett, P. H. and Teller, E. (1938). Adsorption of Gases in Multimolecular Layers. *Journal of the American Chemical Society* 60, 309–319.

Caglayan, B. S. and Aksoylu, A. E. (2013). CO2 adsorption on chemically modified activated carbon. *Journal of Hazardous Materials* 252–253 (0), 19-28.

Cauda, V., Argyo, C., Schlossbauer, A. and Bein, T. (2010). Controlling the delivery kinetics from colloidal mesoporous silica nanoparticles with pH-sensitive gates. *Journal of Materials Chemistry* 20 (21), 4305-4311.

Cenens, J. and Schoonheydt, R. A. (1988). Visible Spectroscopy of Methylene Blue on Hectorite, Laponite B, and Barasym in Aqueous Suspension. *Clay and Clay Minerals* 36 (3), 214-224.

Cestari, A. R., Vieira, E. F. S., Vieira, G. S., da Costa, L. P., Tavares, A. M. G., Loh, W. and Airoldi, C. (2009). The removal of reactive dyes from aqueous solutions using chemically modified mesoporous silica in the presence of anionic surfactant—The temperature dependence and a thermodynamic multivariate analysis. *Journal of Hazardous Materials* 161 (1), 307-316.

Chabani, M., Amrane, A. and Bensmaili, A. (2006). Kinetic modelling of the adsorption of nitrates by ion exchange resin. *Chemical Engineering Journal* 125 (2), 111-117.

Chan, Z., Miao, F., Xiao, Z., Juan, H. and Hongbing, Z. (2007). Effect of doping levels on the pore structure of carbon nanotube/silica xerogel composites. *Materials Letters* 61 (3), 644-647.

Chatterjee, S., Lee, M. W. and Woo, S. H. (2010). Adsorption of congo red by chitosan hydrogel beads impregnated with carbon nanotubes. *Bioresource Technology* 101 (6), 1800-1806.

Chen, C. L., Hu, J., Shao, D. D., Li, J. X. and Wang, X. K. (2009). Adsorption behavior of multiwall carbon nanotube/iron oxide magnetic composites for Ni(II) and Sr(II). *Journal of Hazardous Materials* 164, 923-928.

Choudhary, V., Singh, B. P. and Mathur, R. B. (2013). *Carbon Nanotubes and Their Composites*.

Ciesla, U. and Schüth, F. (1999). Ordered mesoporous materials. *Microporous and Mesoporous Materials* 27 (2–3), 131-149.

Corma, A. (1997). From Microporous to Mesoporous Molecular Sieve Materials and Their Use in Catalysis. *Chemical Reviews* 97 (6), 2373-2420.

Crini, G. (2006). Non-conventional low-cost adsorbents for dye removal: A review. *Bioresource Technology* 97 (9), 1061-1085.

Dąbrowski, A. (2001). Adsorption — from theory to practice. *Advances in Colloid and Interface Science* 93 (1–3), 135-224.

Deng, C., Liu, J., Zhou, W., Zhang, Y.-K., Du, K.-F. and Zhao, Z.-M. (2012). Fabrication of spherical cellulose/carbon tubes hybrid adsorbent anchored with welan gum polysaccharide and its potential in adsorbing methylene blue. *Chemical Engineering Journal* 200–202 (0), 452-458.

Ding, K., Hu, B., Xie, Y., An, G., Tao, R., Zhang, H. and Liu, Z. (2009). A simple route to coat mesoporous SiO2 layer on carbon nanotubes. *Journal of Materials Chemistry* 19 (22), 3725-3731.

Doğan, M., Alkan, M. and Onganer, Y. (2000). Adsorption of methylene blue from aqueous solution onto perlite. *Water, Air, and Soil Pollution* 120 (3-4), 229-248.

Dong, Y., Lu, B., Zang, S., Zhao, J., Wang, X. and Cai, Q. (2010). Removal ofmethylene blue from coloured effluents by adsorption onto SBA-15. *Journal of Chemical Technology and Biotechnology* 86, 616-619.

Dubinin, M. M. (1960). The Potential Theory of Adsorption of Gases and Vapors for Adsorbents with Energetically Nonuniform Surfaces. *Chemical Reviews* 60 (2), 235-241.

Dubinin, M. M. and Radushkevich, L. V. (1947). Equation of the characteristic curve of activated charcoal. *Proceedings of the Academy of Sciences, Physical Chemistry Section*, USSR.

Eder, D. (2010). Carbon Nanotube−Inorganic Hybrids. *Chemical Reviews* 110 (3), 1348-1385.

Eftekhari, S., Habibi-Yangjeh, A. and Sohrabnezhad, S. (2010). Application of AlMCM-41 for competitive adsorption of methylene blue and rhodamine B: Thermodynamic and kinetic studies. *Journal of Hazardous Materials* 178, 349-355.

El-Safty, S. A., Shahat, A. and Awual, M. R. (2011). Efficient adsorbents of nanoporous aluminosilicate monoliths for organic dyes from aqueous solution. *Journal of Colloid and Interface Science* 359 (1), 9-18.

Fagan, S. B., Girao, E. and AG Filho, S. (2006). First principles study of 1, 2-dichlorobenzene adsorption on metallic carbon nanotubes. *International Journal of Quantum Chemistry* 106 (13), 2558-2563.

Fei, B., Qian, B., Yang, Z., Wang, R., Liu, W. C., Mak, C. L. and Xin, J. H. (2008). Coating carbon nanotubes by spontaneous oxidative polymerization of dopamine. *Carbon* 46 (13), 1795-1797.

Feng, L., van Hullebusch, E. D., Rodrigo, M. A., Esposito, G. and Oturan, M. A. (2013). Removal of residual anti-inflammatory and analgesic pharmaceuticals from aqueous systems by electrochemical advanced oxidation processes. A review. *Chemical Engineering Journal* 228 (0), 944-964.

Flanigen, E. M., Khatami, H. and Szymanski, H. A. (1971). Infrared structural studies of zeolite frameworks. In: Molecular Sieve Zeolites. *Advances in Chemistry Series* 101, 201-229.

Foo, K. Y. and Hameed, B. H. (2010). Insights into the modeling of adsorption isotherm systems. *Chemical Engineering Journal* 156 (1), 2-10.

Foo, K. Y. and Hameed, B. H. (2011). Preparation of oil palm (Elaeis) empty fruit bunch activated carbon by microwave-assisted KOH activation for the adsorption of methylene blue. *Desalination* 275 (1–3), 302-305.

Foo, K. Y. and Hameed, B. H. (2012). Adsorption characteristics of industrial solid waste derived activated carbon prepared by microwave heating for methylene blue. *Fuel Processing Technology* 99 (0), 103-109.

Forgacs, E., Cserháti, T. and Oros, G. (2004). Removal of synthetic dyes from wastewaters: a review. *Environment International* 30 (7), 953-971.

Freundlich, H. (1906). *Über die adsorption in lösungen*. Leipzig, Engelmann.

Gatica, S. M., Bojan, J., Stan, G. and Cole, M. W. (2001). Quasi-one- and two-dimensional transitions of gases adsorbed on nanotube bundles. *J. Chem. Phys.* 114, 3765-3769.

Ghosh, D. and Bhattacharyya, K. G. (2002). Adsorption of methylene blue on kaolinite. *Applied Clay Science* 20 (6), 295-300.

Gong, J.-L., Wang, B., Zeng, G.-M., Yang, C.-P., Niu, C.-G., Niu, Q.-Y., Zhou, W.-J. and Liang, Y. (2009). Removal of cationic dyes from aqueous solution using magnetic multi-wall carbon nanotube nanocomposite as adsorbent. *Journal of Hazardous Materials* 164 (2–3), 1517-1522.

Gong, R., Jin, Y., Chen, J., Hu, Y. and Sun, J. (2007). Removal of basic dyes from aqueous solution by sorption on phosphoric acid modified rice straw. *Dyes and Pigments* 73 (3), 332-337.

Gorelikov, I. and Matsuura, N. (2007). Single-Step Coating of Mesoporous Silica on Cetyltrimethyl Ammonium Bromide-Capped Nanoparticles. *Nano Letters* 8 (1), 369-373.

Gregg, S. J. and Sing, K. S. W. (1967). *Adsorption Surface Area and Porosity*. (1st). London, Academic Press.

Gulnaz, O., Kaya, A., Matyar, F. and Arikan, B. (2004). Sorption of basic dyes from aqueous solution by activated sludge. *Journal of Hazardous Materials* 108 (3), 183-188.

Gupta, N., Amritphale, S. S. and Chandra, N. (2010). Removal of Zn (II) from aqueous solution by using hybrid precursor of silicon and carbon. *Bioresource Technology* 101, 3355-3362.

Gupta, V. K., Kumar, R., Nayak, A., Saleh, T. A. and Barakat, M. A. (2013). Adsorptive removal of dyes from aqueous solution onto carbon nanotubes: A review. *Advances in Colloid and Interface Science* 193–194 (0), 24-34.

Gupta, V. K. and Suhas (2009). Application of low-cost adsorbents for dye removal – A review. *Journal of Environmental Management* 90 (8), 2313-2342.

Haghseresht, F. and Lu, G. (1998). Adsorption characteristics of phenolic compounds onto coal-reject-derived adsorbents. *Energy Fuels* 12, 1100-1107.

Hamdaoui, O. (2006). Batch study of liquid-phase adsorption of methylene blue using cedar sawdust and crushed brick. *Journal of Hazardous Materials* 135 (1), 264-273.

Hameed, B. H. (2008). Equilibrium and kinetic studies of methyl violet sorption by agricultural waste. *Journal of Hazardous Materials* 154 (1–3), 204-212.

Hameed, B. H. (2009a). Removal of cationic dye from aqueous solution using jackfruit peel as non-conventional low-cost adsorbent. *Journal of Hazardous Materials* 162 (1), 344-350.

Hameed, B. H. (2009b). Spent tea leaves: A new non-conventional and low-cost adsorbent for removal of basic dye from aqueous solutions. *Journal of Hazardous Materials* 161 (2–3), 753-759.

Hameed, B. H., Mahmoud, D. K. and Ahmad, A. L. (2008). Sorption equilibrium and kinetics of basic dye from aqueous solution using banana stalk waste. *Journal of Hazardous Materials* 158 (2–3), 499-506.

Harkins, W. D. and Jura, E. J. (1944). The decrease of free surface energy as a basis for the development of equations for adsorption isotherms; and The Existance of Two Condensed Phases in Films on Solids. *Journal of Chemical Physics* 12, 112-113.

Hirsch, A. and Vostrowsky, O. (2005). *Functionalization of Carbon Nanotubes*. In Schlüter, A. D. *Functional Molecular Nanostructures*. 245 (193-237). Berlin / Heidelberg: Springer

Ho, K. Y., McKay, G. and Yeung, K. L. (2003). Selective Adsorbents from Ordered Mesoporous Silica. *Langmuir* 19, 3019-3024.

Ho, Y. S. and McKay, G. (1999). Pseudo-second order model for sorption processes. *Process Biochemistry* 34, 451-465.

Hoffmann, F., Cornelius, M., Morell, J. and Froba, M. (2006). Silica-based mesoporous organic-inorganic hybrid materials. *Angewandte Chemie (International ed. in English)* 45 (20), 3216-3251.

Hu, J., Tong, Z., Hu, Z., Chen, G. and Chen, T. (2012). Adsorption of roxarsone from aqueous solution by multi-walled carbon nanotubes. *Journal of Colloid and Interface Science* 377 (1), 355-361.

Huang, C.-H., Chang, K.-P., Ou, H.-D., Chiang, Y.-C. and Wang, C.-F. (2011). Adsorption of cationic dyes onto mesoporous silica. *Microporous and Mesoporous Materials* 141 (1–3), 102-109.

Iijima, S. (1991). Helical microtubules of graphitic carbon. *Nature* 354, 56-58.

Inagaki, S., Fukushima, Y. and Kuroda, K. (1993). Synthesis of highly ordered mesoporous materials from a layered polysilicate. *Journal of the Chemical Society, Chemical Communications* (8), 680-682.

Inglezakis, V. and Poulopoulos, S. (2006). *Adsorption, ion exchange and catalysis: design of operations and environmental applications*. Access Online via Elsevier.

Jaafar, N. F., Abdul Jalil, A., Triwahyono, S., Muhd Muhid, M. N., Sapawe, N., Satar, M. A. H. and Asaari, H. (2012). Photodecolorization of methyl orange over α-Fe2O3-supported HY catalysts: The effects of catalyst preparation and dealumination. *Chemical Engineering Journal* 191 (0), 112-122.

Jalil, A. A., Triwahyono, S., Adam, S. H., Rahim, N. D., Aziz, M. A. A., Hairom, N. H. H., Razali, N. A. M., Abidin, M. A. Z. and Mohamadiah, M. K. A. (2010). Adsorption of methyl orange from aqueous solution onto calcined Lapindo volcanic mud. *Journal of Hazardous Materials* 181 (1–3), 755-762.

Kamarudin, N. H. N., Jalil, A. A., Triwahyono, S., Salleh, N. F. M., Karim, A. H., Mukti, R. R., Hameed, B. H. and Ahmad, A. (2013). Role of 3-aminopropyltriethoxysilane in the preparation of mesoporous silica nanoparticles for ibuprofen delivery: Effect on physicochemical properties. *Microporous and Mesoporous Materials* 180 (0), 235-241.

Kao, K.-C. and Mou, C.-Y. (2013). Pore-expanded mesoporous silica nanoparticles with alkanes/ethanol as pore expanding agent. *Microporous and Mesoporous Materials* 169 (0), 7-15.

Karim, A. H., Jalil, A. A., Triwahyono, S., Sidik, S. M., Kamarudin, N. H. N., Jusoh, R., Jusoh, N. W. C. and Hameed, B. H. (2012). Amino modified mesostructured silica nanoparticles for efficient adsorption of methylene blue. *Journal of Colloid and Interface Science* 386, 307-314.

Klinowski, J. and Barrie, P. J. (1989). *Recent Advances in Zeolite Science*. Cambridge, Elsevier Science.

Kondratyuk, P. and Yates, J. T. (2007). Molecular views of physical adsorption inside and outside of single-wall carbon manotubes. *Acc. Chem. Res.* 40, 995-1004.

Kresge, C. T., Leonowicz, M. E., Roth, W. J., Vartuli, J. C. and Beck, J. S. (1992). Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism. *Nature* 359 (6397), 710-712.

Krug, R., Hunter, W. and Grieger, R. (1976). Enthalpy-entropy compensation. 1. Some fundamental statistical problems associated with the analysis of van't Hoff and Arrhenius data. *The Journal of Physical Chemistry* 80 (21), 2335-2341.

Kruk, M. and Jaroniec, M. (2001). Gas adsorption characterization of ordered organic-inorganic nanocomposite materials. *Chemistry of Materials* 13 (10), 3169-3183.

Kuo, C.-Y., Wu, C.-H. and Wu, J.-Y. (2008). Adsorption of direct dyes from aqueous solutions by carbon nanotubes: Determination of equilibrium, kinetics and thermodynamics parameters. *Journal of Colloid and Interface Science* 327 (2), 308-315.

Kupfer, A., Aeschlimann, C., Wermuth, B. and Cerny, T. (1994). Prophylaxis and reversal of ifosfamide encephalopathy with methylene-blue. *Lancet* 343, 763-764.

Lagergren, S. (1898). About the theory of so-called adsorption of soluble substances, Kungliga Svenska Vetenskapsakademiens. *Handlingar*.

Landers, J., Gor, G. Y. and Neimark, A. V. (2013). Density functional theory methods for characterization of porous materials. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 437, 3-32.

Langmuir, I. (1917). The Constitution and Fundamental Properties of Solids and Liquids. Part II. Liquids. *Journal of the American Chemical Society* 39 (9), 1848-1906.

Lastoskie, C., Gubbins, K. E. and Quirke, N. (1993). Pore size distribution analysis of microporous carbons: a density functional theory approach. *The Journal of Physical Chemistry* 97 (18), 4786-4796.

Li, D. and Wang, H. (2010). Recent developments in reverse osmosis desalination membranes. *Journal of Materials Chemistry* 20 (22), 4551-4566.

Li, X., Chen, S., Li, L., Quan, X. and Zhao, H. (2014). Electrochemically enhanced adsorption of nonylphenol on carbon nanotubes: Kinetics and isotherms study. *Journal of Colloid and Interface Science* 415 (0), 159-164.

Li, Y.-L., Qiao, X.-H., Feng, J.-M., Zhong, X.-H., Zhang, L.-H., Qian, L.-P. and Hou, F. (2009). Synthesis of highly uniform silica-shelled carbon nanotube coaxial fibers from catalytic gas-flow reactions viain situ deposition of silica. *Journal of Materials Chemistry* 19 (34), 6137-6142.

Li, Y., Du, Q., Liu, T., Peng, X., Wang, J., Sun, J., Wang, Y., Wu, S., Wang, Z., Xia, Y. and Xia, L. (2013). Comparative study of methylene blue dye adsorption onto activated carbon, graphene oxide, and carbon nanotubes. *Chemical Engineering Research and Design* 91 (2), 361-368.

Limousin, G., Gaudet, J. P., Charlet, L., Szenknect, S., Barthès, V. and Krimissa, M. (2007). Sorption isotherms: A review on physical bases, modeling and measurement. *Applied Geochemistry* 22 (2), 249-275.

Lin, S., Song, Z., Che, G., Ren, A., Li, P., Liu, C. and Zhang, J. (2014). Adsorption behavior of metal–organic frameworks for methylene blue from aqueous solution. *Microporous and Mesoporous Materials* 193 (0), 27-34.

Lin, T., Bajpai, V., Ji, T. and Dai, L. (2003). Chemistry of Carbon Nanotubes. *Australian Journal of Chemistry* 56 (7), 635-651.

Long, R. Q. and Yang, R. T. (2001). Carbon nanotubes as superior sorbent for dioxin removal. *J. Am. Chem. Soc.* 123, 2058-2059.

Low, K. S., Lee, C. K. and Tan, K. K. (1995). Biosorption of basic dyes by water hyacinth roots. *Bioresource Technology* 52 (1), 79-83.

Lowell, S., Shields, J., Charalambous, G. and Manzione, J. (1982). Adsorbate cross-sectional area as a function of the BET C constant. *Journal of Colloid and Interface Science* 86 (1), 191-195.

Lu, C., Chiu, H. and Liu, C. (2006). Removal of zinc (II) from aqueous solution by purified carbon nanotubes: kinetics and equilibrium studies. *Industrial & Engineering Chemistry Research* 45 (8), 2850-2855.

Lu, C. and Su, F. (2007). Adsorption of natural organic matter by carbon nanotubes. *Separation and Purification Technology* 58 (1), 113-121.

Lu, C. S. and Chiu, H. S. (2006). Adsorption of zinc(II) fromwater with purified carbon nanotubes. *Chem. Eng. Sci.* 61, 138-145.

Luther, S., Brogfeld, N., Kim, J. and Parsons, J. G. (2013). Study of the thermodynamics of chromium(III) and chromium(VI) binding to iron(II/III)oxide or magnetite or ferrite and magnanese(II) iron (III) oxide or jacobsite or manganese ferrite nanoparticles. *Journal of Colloid and Interface Science* 400 (0), 97-103.

Madrakian, T., Afkhami, A., Ahmadi, M. and Bagheri, H. (2011). Removal of some cationic dyes from aqueous solutions using magnetic-modified multi-walled carbon nanotubes. *Journal of Hazardous Materials* 196 (0), 109-114.

Marungrueng, K. and Pavasant, P. (2007). High performance biosorbent *Caulerpa lentillifera* for basic dye removal. *Bioresource Technology* 98 (8), 1567-1572.

Maurya, N. S., Mittal, A. K., Cornel, P. and Rother, E. (2006). Biosorption of dyes using dead macro fungi: effect of dye structure, ionic strength and pH. *Bioresource Technology* 97 (3), 512-521.

McKay, G., Porter, J. and Prasad, G. (1999). The removal of dye colours from aqueous solutions by adsorption on low-cost materials. *Water, Air, and Soil Pollution* 114 (3-4), 423-438.

McKay, G., Ramprasad, G. and Mowli, P. P. (1986). Equilibrium studies for the adsorption of dyestuffs from aqueous solutions by low-cost materials. *Water, Air, and Soil Pollution* 29 (3), 273-283.

Méhn, D., Brunel, D., Galarneau, A., Perri, C., Fonseca, A., Urbán, M., Kónya, Z., Kiricsi, I. and Nagy, J. B. (2004). *Synthesis of carbon nanotubes with tailor made diameter in the channels of micelle-templated silicas*. In E. van Steen, I. M. C. and Callanan, L. H. *Studies in Surface Science and Catalysis*. 154 (911-916): Elsevier.

Messina, P. V. and Schulz, P. C. (2006). Adsorption of reactive dyes on titania–silica mesoporous materials. *Journal of Colloid and Interface Science* 299 (1), 305-320.

Meynen, V., Cool, P. and Vansant, E. F. (2009). Verified syntheses of mesoporous materials. *Microporous and Mesoporous Materials* 125 (3), 170-223.

Mezohegyi, G., van der Zee, F. P., Font, J., Fortuny, A. and Fabregat, A. (2012). Towards advanced aqueous dye removal processes: A short review on the versatile role of activated carbon. *Journal of Environmental Management* 102 (0), 148-164.

Mishra, A. K., Arockiadoss, T. and Ramaprabhu, S. (2010). Study of removal of azo dye by functionalized multi walled carbon nanotubes. *Chemical Engineering Journal* 162 (3), 1026-1034.

Mittal, A., Mittal, J., Malviya, A., Kaur, D. and Gupta, V. K. (2010). Decoloration treatment of a hazardous triarylmethane dye, Light Green SF (Yellowish) by waste material adsorbents. *Journal of Colloid and Interface Science* 342, 518-527.

Monnier, A., Schüth, F., Huo, Q., Kumar, D., Margolese, D., Maxwell, R. S., Stucky, G. D., Krishnamurty, M., Petroff, P., Firouzi, A., Janicke, M. and B.F. Chmelka (1993). *Science* 261, 1299.

Moriguchi, I., Honda, M., Ohkkubo, T., Mawatari, Y. and Teraoka, Y. (2004). Adsorption and photocatalytic decomposition of methylene blue on mesoporous metallosocates. *Catalysis Today* 90, 297-303.

Namasivayam, C. and Sumithra, S. (2005). Removal of direct red 12B and methylene blue from water by adsorption onto Fe (III)/Cr (III) hydroxide, an industrial solid waste. *Journal of Environmental Management* 74 (3), 207-215.

Ncibi, M., Hamissa, A., Fathallah, A., Kortas, M., Baklouti, T., Mahjoub, B. and Seffen, M. (2009). Biosorptive uptake of methylene blue using Mediterranean green alga *Enteromorpha* spp. *Journal of Hazardous Materials* 170 (2), 1050-1055.

Nollet, H., Roels, M., Lutgen, P., Van der Meeren, P. and Verstraete, W. (2003). Removal of PCBs from wastewater using fly ash. *Chemosphere* 53 (6), 655-665.

Ofomaja, A. E. (2007). Sorption dynamics and isotherm studies of methylene blue uptake on to palm kernel fibre. *Chemical Engineering Journal* 126 (1), 35-43.

Oguzie, E., Okolue, B., Ebenso, E., Onuoha, G. and Onuchukwu, A. (2004). Evaluation of the inhibitory effect of methylene blue dye on the corrosion of aluminium in hydrochloric acid. *Materials Chemistry and Physics* 87 (2), 394-401.

Oladoja, N. A. and Aliu, Y. D. (2009). Snail shell as coagulant aid in the alum precipitation of malachite green from aqua system. *Journal of Hazardous Materials* 164 (2–3), 1496-1502.

Oz, M., Lorke, D. E. and Petroianu, G. A. (2009). Methylene blue and Alzheimer's disease. *Biochemical Pharmacology* 78, 927-932.

Ozdemir, F. A., Demirata, B. and Apak, R. (2009). Adsorptive removal of methylene blue from simulated dyeing wastewater with melamine-formaldehyde-urea resin. *Journal of Applied Polymer Science* 112 (6), 3442-3448.

Paria, S. and Khilar, K. C. (2004). A review on experimental studies of surfactant adsorption at the hydrophilic solid–water interface. *Advances in Colloid and Interface Science* 110 (3), 75-95.

Ponnusami, V., Vikram, S. and Srivastava, S. (2008). Guava *Psidium guajava* leaf powder: Novel adsorbent for removal of methylene blue from aqueous solutions. *Journal of Hazardous Materials* 152 (1), 276-286.

Popov, V. N. (2004). Carbon nanotubes: properties and application. *Materials Science & Engineering, R: Reports* 43 (3), 61-102.

Prouzet, E., Cot, F., Nabias, G., Larbot, A., Kooyman, P. and Pinnavaia, T. J. (1999). Assembly of mesoporous silica molecular sieves based on nonionic ethoxylated sorbitan esters as structure directors. *Chemistry of Materials* 11 (6), 1498-1503.

Pyrzynska, K. (2007). Application of carbon sorbents for the concentration and separation of metal ions. *Analytical Sciences* 23 (6), 631.

Pyrzynska, K. (2010). Carbon nanostructures for separation, preconcentration and speciation of metal ions. *TrAC Trends in Analytical Chemistry* 29 (7), 718-727.

Qu, S., Huang, F., Yu, S., Chen, G. and Kong, J. (2008). Magnetic removal of dyes from aqueous solution using multi-walled carbon nanotubes filled with Fe2O3 particles. *Journal of Hazardous Materials* 160 (2–3), 643-647.

Ren, X., Chen, C., Nagatsu, M. and Wang, X. (2011). Carbon nanotubes as adsorbents in environmental pollution management: A review. *Chemical Engineering Journal* 170 (2–3), 395-410.

Riha, P. D., Bruchey, A. K., Echevarria, D. J. and Gonzalez-Lima, F. (2005). Memory facilitation bymethylene blue: dose dependent effect onbehavior and brain oxygen consumption. *European Journal of Pharmacolology* 511, 151-158.

Robinson, T., Chandran, B. and Nigam, P. (2002). Studies on desorption of individual textile dyes and a synthetic dye effluent from dye-adsorbed agricultural residues using solvents. *Bioresource Technology* 84 (3), 299-301.

Rodríguez, A., Ovejero, G., Sotelo, J. L., Mestanza, M. and García, J. (2010). Adsorption of dyes on carbon nanomaterials from aqueous solutions. *Journal of Environmental Science and Health, Part A* 45 (12), 1642-1653.

Salvador, F., Sánchez-Jiménez, C., Sánchez-Montero, M. J. and Salvador, A. (2002). *A review of the application of the BET equation to experimental data: the C parameter*. In F. Rodriguez-Reinoso, B. M. J. R. and Unger, K. *Studies in Surface Science and Catalysis*. 144 (379-386): Elsevier.

Sapawe, N., Jalil, A. A. and Triwahyono, S. (2013a). One-pot electro-synthesis of ZrO2–ZnO/HY nanocomposite for photocatalytic decolorization of various dye-contaminants. *Chemical Engineering Journal* 225 (0), 254-265.

Sapawe, N., Jalil, A. A., Triwahyono, S., Shah, M. I. A., Jusoh, R., Salleh, N. F. M., Hameed, B. H. and Karim, A. H. (2013b). Cost-effective microwave rapid synthesis of zeolite NaA for removal of methylene blue. *Chemical Engineering Journal* 229, 388-398.

Shahryari, Z., Goharrizi, A. S. and Azadi, M. (2010). Experimental study of methylene blue adsorption from aqueous solutions onto carbon nano tubes. *Int.J.Water Resour.Environ.Eng.* 2 (2), 16-28.

Sidik, S. M., Jalil, A. A., Triwahyono, S., Adam, S. H., Satar, M. A. H. and Hameed, B. H. (2012). Modified oil palm leaves adsorbent with enhanced hydrophobicity for crude oil removal. *Chemical Engineering Journal* 203 (0), 9-18.

Sing, K. S. W., Everett, D. H., Haul, R. A. W., Moscou, L., Pierotti, R. A., Rouquerol, J. and Siemieniewska, T. (1985). International Union of Pure Commission on Colloid and Surface Chemistry Including Catalysis: Reporting Physisorption Data for Gas / Solid Systems with Special Reference to the Determination of Surface Area and Porosity Area. *Pure & Applied Chemistry* 57 (4), 603-619.

Slowing, I. I., Trewyn, B. G. and Lin, V. S. Y. (2007). Mesoporous Silica Nanoparticles for Intracellular Delivery of Membrane-Impermeable Proteins. *Journal of the American Chemical Society* 129 (28), 8845-8849.

Slowing, I. I., Vivero-Escoto, J. L., Wu, C.-W. and Lin, V. S. Y. (2008). Mesoporous silica nanoparticles as controlled release drug delivery and gene transfection carriers. *Advanced Drug Delivery Reviews* 60 (11), 1278-1288.

Smart, S. K., Cassady, A. I., Lu, G. Q. and Martin, D. J. (2006). The biocompatibility of carbon nanotubes. *Carbon* 44 (6), 1034-1047.

Sobolkina, A., Mechtcherine, V., Bellmann, C., Khavrus, V., Oswald, S., Hampel, S. and Leonhardt, A. (2014). Surface properties of CNTs and their interaction with silica. *Journal of Colloid and Interface Science* 413 (0), 43-53.

Soler-Illia, G. J. d. A. A., Sanchez, C., Lebeau, B. and Patarin, J. (2002). Chemical Strategies To Design Textured Materials: from Microporous and Mesoporous Oxides to Nanonetworks and Hierarchical Structures. *Chemical Reviews* 102 (11), 4093-4138.

Son, W.-J., Choi, J.-S. and Ahn, W.-S. (2008). Adsorptive removal of carbon dioxide using polyethyleneimine-loaded mesoporous silica materials. *Microporous and Mesoporous Materials* 113 (1–3), 31-40.

Stavropoulos, G. and Zabaniotou, A. (2005). Production and characterization of activated carbons from olive-seed waste residue. *Microporous and Mesoporous Materials* 82 (1), 79-85.

Sui, K., Li, Y., Liu, R., Zhang, Y., Zhao, X., Liang, H. and Xia, Y. (2012). Biocomposite fiber of calcium alginate/multi-walled carbon nanotubes with enhanced adsorption properties for ionic dyes. *Carbohydrate Polymers* 90 (1), 399-406.

Tasis, D., Tagmatarchis, N., Bianco, A. and Prato, M. (2006). *Chemical Reviews* 106, 1105.

Temkin, M. I. and Pyzhev, V. (1940). Kinetic of ammonia synthesis on promoted iron catalyst. *Acta Physicochimica URSS* 12, 327-356.

Trojanowicz, M. (2006). Analytical applications of carbon nanotubes: a review. *TrAC Trends in Analytical Chemistry* 25 (5), 480-489.

Uddin, M. T., Islam, M. A., Mahmud, S. and Rukanuzzaman, M. (2009). Adsorptive removal of methylene blue by tea waste. *Journal of Hazardous Materials* 164 (1), 53-60.

Vargas, A. M. M., Cazetta, A. L., Kunita, M. H., Silva, T. L. and Almeida, V. C. (2011). Adsorption of methylene blue on activated carbon produced from flamboyant pods (Delonix regia): Study of adsorption isotherms and kinetic models. *Chemical Engineering Journal* 168, 722-730.

Vartuli, J. C., Schmitt, K. D., Kresge, C. T., Roth, W. J., Leonowicz, M. E., McCullen, S. B., Hellring, S. D., Beck, J. S. and Schlenker, J. L. (1994). Effect of Surfactant/Silica Molar Ratios on the Formation of Mesoporous

Molecular Sieves: Inorganic Mimicry of Surfactant Liquid-Crystal Phases and Mechanistic Implications. *Chemistry of Materials* 6 (12), 2317-2326.

Vila, M., Hueso, J. L., Manzano, M., Izquierdo-Barba, I., de Andres, A., Sanchez-Marcos, J., Prieto, C. and Vallet-Regi, M. (2009). Carbon nanotubes-mesoporous silica composites as controllable biomaterials. *Journal of Materials Chemistry* 19 (41), 7745-7752.

Wainwright, M. (2000). Methylene blue derivatives - suitable photoantimicrobials for blood product disinfection. *International Journal of Antimicrobial Agents* 16, 381 - 394.

Walcarius, A. and Mercier, L. (2010). Mesoporous organosilica adsorbents: nanoengineered materials for removal of organic and inorganic pollutants. *Journal of Materials Chemistry* 20 (22), 4478-4511.

Wan Ngah, W. S. and Hanafiah, M. A. K. M. (2008). Adsorption of copper on rubber (Hevea brasiliensis) leaf powder: Kinetic, equilibrium and thermodynamic studies. *Biochemical Engineering Journal* 39 (3), 521-530.

Wan, Y. and Zhao, D. (2007). On the Controllable Soft-Templating Approach to Mesoporous Silicates. *Chemical Reviews* 107 (7), 2821-2860.

Wang, J.-P., Yang, H.-C. and Hsieh, C.-T. (2010). Adsorption of Phenol and Basic Dye on Carbon Nanotubes/Carbon Fabric Composites from Aqueous Solution. *Separation Science and Technology* 46 (2), 340-348.

Wang, J., Sugawara-Narutaki, A., Shimojima, A. and Okubo, T. (2012a). Biphasic synthesis of colloidal mesoporous silica nanoparticles using primary amine catalysts. *Journal of Colloid and Interface Science* 385 (1), 41-47.

Wang, L., Shan, Z., Zhang, Z., Wei, F. and Xiao, F.-S. (2009). One-pot hydrothermal synthesis of mesostructured silica nanotube. *Journal of Colloid and Interface Science* 335 (2), 264-267.

Wang, S. (2009). Ordered mesoporous materials for drug delivery. *Microporous and Mesoporous Materials* 117 (1–2), 1-9.

Wang, S. and Li, H. (2006). Structure directed reversible adsorption of organic dye on mesoporous silica in aqueous solution. *Microporous and Mesoporous Materials* 97, 21-26.

Wang, S., Li, H. and Xu, L. (2006). Application of zeolite MCM-22 for basic dye removal from wastewater. *Journal of Colloid and Interface Science* 295, 71-78.

Wang, S., Ng, C. W., Wang, W., Li, Q. and Hao, Z. (2012b). Synergistic and competitive adsorption of organic dyes on multiwalled carbon nanotubes. *Chemical Engineering Journal* 197 (0), 34-40.

Weber, W. J. and Morris, J. C. (1963). Kinetics of adsorption on carbon from solution. *Journal of Sanitary Engineering Division, American Society of Civil Engineers* 89, 31-60.

Woolard, C., Strong, J. and Erasmus, C. (2002). Evaluation of the use of modified coal ash as a potential sorbent for organic waste streams. *Applied Geochemistry* 17 (8), 1159-1164.

Wu, B., Hu, D., Kuang, Y., Liu, B., Zhang, X. and Chen, J. (2009). Functionalization of Carbon Nanotubes by an Ionic-Liquid Polymer: Dispersion of Pt and PtRu Nanoparticles on Carbon Nanotubes and Their Electrocatalytic Oxidation of Methanol. *Angewandte Chemie, International Edition in English* 48 (26), 4751-4754.

Yadava, K. P., Tyagi, B. S. and Singh, V. N. (1991). Effect of temperature on the removal of lead(II) by adsorption on China clay and wollastonite. *Journal of Chemical Technology & Biotechnology* 51 (1), 47-60.

Yanagisawa, T., Shimizu, T., Kuroda, K. and Kato, C. (1990). The preparation of alkyltrimethylammonium-kanemite complexes and their conversion to mocroporous materials. *Bulletin of the Chemical Society of Japan* 63 (4), 988-992.

Yang, H. and Feng, Q. (2010). Characterization of pore-expanded amino-functionalized mesoporous slica directly synthesized with dimethyldecylamine and its application for decolorization of sulphonated azo dyes. *Journal of hazardous Materials* 180, 106-114.

Yao, Y., Bing, H., Feifei, X. and Xiaofeng, C. (2011). Equilibrium and kinetic studies of methyl orange adsorption on multiwalled carbon nanotubes. *Chemical Engineering Journal* 170 (1), 82-89.

Yao, Y., Xu, F., Chen, M., Xu, Z. and Zhu, Z. (2010a). *5th IEEE Int. Conf. Nano/Micro Engineered and Molecular Systems*, Xiamen, China.

Yao, Y., Xu, F., Chen, M., Xu, Z. and Zhu, Z. (2010b). Adsorption behavior of methylene blue on carbon nanotubes. *Bioresource Technology* 101 (9), 3040-3046.

Yokoi, T., Kubota, Y. and Tatsumi, T. (2012). Amino-functionalized mesoporous silica as base catalyst and adsorbent. *Applied Catalysis A: General* 421–422 (0), 14-37.

Yu, Y., Yu, J. C., Yu, J.-G., Kwok, Y.-C., Che, Y.-K., Zhao, J.-C., Ding, L., Ge, W.-K. and Wong, P.-K. (2005). Enhancement of photocatalytic activity of mesoporous TiO2 by using carbon nanotubes. *Applied Catalysis A: General* 289 (2), 186-196.

Zanjanchi, M. A., Golmojdeh, H. and Arvand, M. (2009). Enhanced adsorptive and photocatalytic achievements in removal of methylene blue by incorporating tungstophosphoric acid–TiO2 into MCM-41. *Journal of Hazardous Materials* 169, 233-239.

Zeng, Y.-L., Huang, Y.-F., Jiang, J.-H., Zhang, X.-B., Tang, C.-R., Shen, G.-L. and Yu, R.-Q. (2007). Functionalization of multi-walled carbon nanotubes with poly(amidoamine) dendrimer for mediator-free glucose biosensor. *Electrochemistry Communications* 9 (1), 185-190.

Zhang, A., Hou, K., Gu, L., Dai, C., Liu, M., Song, C. and Guo, X. (2012). Synthesis of Silica Nanotubes with Orientation Controlled Mesopores in Porous Membranes via Interfacial Growth. *Chemistry of Materials* 24 (6), 1005-1010.

Zhang, M., Wu, Y., Feng, X., He, X., Chen, L. and Zhang, Y. (2010). Fabrication of mesoporous silica-coated CNTs and application in size-selective protein separation. *Journal of Materials Chemistry* 20 (28), 5835-5842.

Zhao, D., Feng, J., Huo, Q., Melosh, N., Fredrickson, G. H., Chmekka, B. F. and Stucky, G. D. (1998a). *Science* 279, 548-552.

Zhao, D., Huo, Q., Feng, J., Chmelka, B. F. and Stucky, G. D. (1998b). Nonionic Triblock and Star Diblock Copolymer and Oligomeric Surfactant Syntheses of Highly Ordered, Hydrothermally Stable, Mesoporous Silica Structures. *Journal of the American Chemical Society* 120 (24), 6024-6036.

Zhou, H., Zhang, C., Li, H. and Du, Z. (2011). Fabrication of silica nanoparticles on the surface of functionalized multi-walled carbon nanotubes. *Carbon* 49 (1), 126-132.