

**DEVELOPMENT OF POLYSACCHARIDE
DERIVED CARBON AEROGELS FOR THE
REMEDICATION OF PHARMACEUTICALS
CONTAMINATED WATER**

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**DEVELOPMENT OF POLYSACCHARIDE DERIVED CARBON
AEROGELS FOR THE REMEDIATION OF PHARMACEUTICALS
CONTAMINATED WATER**

by

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TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENT	ii
TABLE OF CONTENTS	iii
LIST OF TABLES	viii
LIST OF FIGURES	xi
LIST OF PLATES	xiii
LIST OF ABBREVIATIONS	xiv
LIST OF SYMBOLS	xvi
ABSTRAK	xviii
ABSTRACT	xix
CHAPTER ONE – INTRODUCTION	
1.1 An overview of the current development and applications of carbon	1
1.2 Problem statement	2
1.3 Research objectives	4
1.4 Scope of study	4
1.5 Significance of study	5
1.6 Organisation of the thesis	6
CHAPTER TWO – LITERATURE REVIEW	
2.1 Carbon aerogel	8
2.1.1 Definition and evolution	8
2.1.2 Specific features of carbon aerogel	12

2.1.3	Distinctive properties and applications of carbon aerogel	13
2.1.3(a)	Electrochemical	13
2.1.3(b)	Catalyst	14
2.1.3(c)	Thermal insulator	15
2.1.3(d)	Hydrogen storage	16
2.1.3(e)	Adsorption	17
2.2	Carbon aerogel preparation procedure	21
2.2.1	Sol-gel process	22
2.2.2	Aging	23
2.2.3	Drying	24
2.2.4	Carbonization	25
2.2.5	Activation	26
2.3	Polysaccharides	27
2.3.1	Carrageenan	27
2.3.2	Pectin	30
2.3.3	Sago	31
2.3.4	Guar gum	32
2.3.5	Konjac gum	32
2.3.6	Xanthan gum	33
2.3.7	Psyllium husk	33
2.3.8	Sodium alginate	34
2.4	Pharmaceutical contaminants	35
2.4.1	Paracetamol	43
2.4.2	Metformin	44
2.4.3	Amoxicillin	45

2.4.4	Caffeine	45
2.5	Pharmaceutical treatment methods	46
2.6	Adsorption technology	52
2.6.1	Adsorption isotherm	56
2.6.2	Adsorption kinetic	60
2.6.3	Adsorption thermodynamic	61
2.7	Summary	62
CHAPTER THREE – MATERIALS AND METHODOLOGY		
3.1	Materials and chemicals	64
3.2	Pharmaceutical pollutants	66
3.3	Carbon aerogel synthesis	69
3.4	Carbonization system and analytical instruments	70
3.4.1	Carbonization system	70
3.4.2	Analytical instrument	74
3.5	Batch adsorption study	76
3.6	Adsorption isotherm	79
3.7	Adsorption kinetics	80
3.8	Thermodynamic study	81
3.9	Characterization systems	82
3.9.1	Scanning electron microscopy (SEM)	82
3.9.2	Fourier transform infrared spectroscopy (FTIR)	82
3.9.3	Surface physical analysis	83
3.9.4	Determination of pH_{ZPC}	84

CHAPTER FOUR – RESULTS AND DISCUSSION

4.1	Optimization of the carbon aerogel preparation parameters	85
4.1.1	Effect of activation agent	85
4.1.2	Effect of impregnation ratio (<i>IR</i>)	88
4.1.3	Effect of activation temperature	91
4.1.4	Effect of activation time	94
4.2	Physical, chemical and physiochemical characterizations	97
4.2.1	Surface morphology	97
4.2.2	Surface functional groups	102
4.2.3	Porosity structure	108
4.3	Batch adsorption studies	110
4.3.1	Effect of initial concentrations and contact time	110
4.3.2	Effect of solution pH	118
4.4	Adsorption isotherm	123
4.5	Adsorption kinetic modelling	127
4.6	Adsorption thermodynamics	140

CHAPTER FIVE – CONCLUSIONS AND RECOMMENDATIONS

5.1	Conclusions	144
5.2	Recommendations	146

REFERENCES	147
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APPENDICES

APPENDIX A	Point of zero charge of (a) CCA (b) PCA (c) SOCA (d) GGCA (e) KGCA (f) XGCA (g) PHCA and (h) SACA
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- APPENDIX B Effect of adsorbent dosage on the adsorptive uptake of PCM, MTF, AMX and CAF.
- APPENDIX C Non-linear isotherm plots for the adsorption of (a) PCM onto CCA (b) PCM onto PCA (c) MTF onto SOCA (d) MTF onto GGCA (e) AMX onto KGCA (f) AMX onto XGCA (g) CAF onto PHCA and (h) CAF onto SACA
- APPENDIX D Plots of (a) pseudo-first-order, (b) pseudo-second-order and (c) Elovich kinetics models for the adsorption of PCM, MTF, AMX and CAF

LIST OF PUBLICATIONS AND AWARDS

LIST OF TABLES

	Page
Table 2.1 Historical evolution of aerogels	10
Table 2.2 Available applications of carbon aerogel	18
Table 2.3 Adsorption capability of carbon aerogels for different water pollutants	19
Table 2.4 Summary of the conventional drying methods used for carbon gels	25
Table 2.5 A comprehensive list of carbon aerogels	28
Table 2.6 Compilation of hospital effluent parameters	37
Table 2.7 Compiled therapeutic classes and concentration range measured in the effluent of health care centres	38
Table 2.8 Current scenario of the pharmaceutical pollutants in the Malaysian aquatic environment	41
Table 2.9 The advantages and disadvantages of the current pharmaceutical remediation technologies	50
Table 2.10 A comprehensive summary of the pharmaceutical treatment via adsorption process	53
Table 2.11 The advantages and disadvantages of the application of the carbon based adsorbent (Zhang <i>et al.</i> , 2017)	58
Table 3.1 List of chemicals applied in this work	65
Table 3.2 Raw precursors required for preparation of carbon aerogels	65
Table 3.3 List of instruments applied in this work	66
Table 3.4 Molecular characteristics of paracetamol, metformin, amoxicillin and caffeine	68
Table 3.5 Sol-gel precursors and preparation parameters	69

Table 3.6	The experiments employed for each polysaccharide derived carbon aerogels	71
Table 3.7	Operating conditions for the batch adsorption systems	78
Table 4.1	Optimal experimental conditions for the preparation of carbon aerogels	97
Table 4.2	Surface physical properties of CCA, PCA, SOCA, GGCA, KGCA, XGCA, PHCA and SACA	109
Table 4.3	Comparison of BET surface area for different carbon aerogels	110
Table 4.4	Treatment time of pharmaceutical compounds onto different adsorbents	117
Table 4.5	Isotherm parameters for the adsorption of PCM onto CCA and PCA, MTF onto SOCA and GGCA, AMX onto XGCA and KGCA and CAF onto PHCA and SACA at 30°C	125
Table 4.6	A comparison of the monolayer adsorption capacity of PCM, MTF, AMX and CAF onto different adsorbents	128
Table 4.7	Pseudo-first-order, pseudo-second-order and Elovich kinetic parameters for the adsorption of PCM onto CCA	131
Table 4.8	Pseudo-first-order, pseudo-second-order and Elovich kinetic parameters for the adsorption of PCM onto PCA	132
Table 4.9	Pseudo-first-order, pseudo-second-order and Elovich kinetic parameters for the adsorption of MTF onto SOCA	133
Table 4.10	Pseudo-first-order, pseudo-second-order and Elovich kinetic parameters for the adsorption of MTF onto GGCA	134
Table 4.11	Pseudo-first-order, pseudo-second-order and Elovich kinetic parameters for the adsorption of AMX onto KGCA	135
Table 4.12	Pseudo-first-order, pseudo-second-order and Elovich kinetic parameters for the adsorption of AMX onto XGCA	136

Table 4.13	Pseudo-first-order, pseudo-second-order and Elovich kinetic parameters for the adsorption of CAF onto PHCA	137
Table 4.14	Pseudo-first-order, pseudo-second-order and Elovich kinetic parameters for the adsorption of CAF onto SACA	138
Table 4.15	Thermodynamic parameters for the adsorption of PCM, MTF, AMX and CAF	141

LIST OF FIGURES

	Page
Figure 2.1 The classifications of aerogel (Du <i>et al.</i> , 2013)	12
Figure 2.2 General procedure for the development of carbon aerogel	21
Figure 2.3 Representation of the sol-gel process	23
Figure 2.5 Basic terminology of adsorption process	52
Figure 3.2 Schematic drawing of the carbonization system	74
Figure 3.3 Calibration curve of (a) PCM, (b) MTF, (c) AMX and (d) CAF	75
Figure 3.1 Flowchart of research activities	67
Figure 4.1 Effect of activation agent onto the adsorption uptake of PCM onto CCA and PCA, MTF onto SOCA and GGCA, AMX onto KGCA and XGCA and CAF onto PHCA and SACA (Preparation conditions: <i>IR</i> : 1:1; Activation temperature: 800 °C; Activation time: 1 hour)	86
Figure 4.2 Effect of <i>IR</i> on the adsorptive uptake of (a) AMX onto KGCA and XGCA (b) CAF onto PHCA and SACA (Preparation conditions: Activation temperature: 800 °C; Activation time: 1 hour)	90
Figure 4.3 Effect of carbonization temperature on the adsorptive uptake of (a) PCM onto CCA and PCA (b) MTF onto SOCA and GGCA (c) AMX onto KGCA and XGCA (d) CAF onto PHCA and SACA (Activation time: 1 hour)	92
Figure 4.4 Effect of activation time on the adsorptive uptake of (a) PCM onto CCA and PCA (b) MTF onto SOCA and GGCA (c) AMX onto KGCA and XGCA (d) CAF onto PHCA and	95
Figure 4.6 Effects of initial concentration and contact time for the adsorptive uptake of PCM onto (a) CCA and (b) PCA (Temperature: 30°C; Adsorbent dosage: 0.05 g / 200 mL)	111
Figure 4.7 Effects of initial concentration and contact time for the adsorptive uptake of MTF onto (a) SOCA and (b) GGCA (Temperature: 30°C; Adsorbent dosage: 0.05 g / 200 mL)	112

Figure 4.8	Effects of initial concentration and contact time for the adsorptive uptake of AMX onto (a) KGCA and (b) XGCA (Temperature: 30°C; Adsorbent dosage: 0.05 g / 200 mL)	113
Figure 4.9	Effects of initial concentration and contact time for the adsorptive uptake of CAF onto (a) PHCA and (b) SACA (Temperature: 30°C; Adsorbent dosage: 0.05 g / 200 mL)	114
Figure 4.10	Effect of solution pH on the adsorptive uptake of PCM onto CCA and PCA at 30 °C (Adsorbate concentration: 300 mg/L; adsorbent dosage: 0.05 g / 200 mL)	119
Figure 4.11	Effect of solution pH on the adsorptive uptake of MTF onto SOCA and GGCA at 30 °C (Adsorbent concentration: 300 mg/L; adsorbent dosage: 0.05 g / 200 mL)	120
Figure 4.12	Effect of solution pH on the adsorptive uptake of AMX onto KGCA and XGCA at 30 °C (Adsorbate concentration: 300 mg/L; adsorbent dosage: 0.05 g / 200 mL)	121
Figure 4.13	Effect of solution pH on the adsorptive uptake of CAF onto PHCA and SACA at 30 °C (Adsorbate concentration: 300 mg/L; adsorbent dosage: 0.05 g / 200 mL)	122

LIST OF PLATES

	Page
Plate 4.1 SEM images of (a) CCA (b) PCA (c) SOCA (d) GGCA (e) KGCA (f) XGCA (g) PHCA and (h) SACA	100

LIST OF ABBREVIATIONS

AC	Activated carbon
AMX	Amoxicillin
BET	Brunauer-Emmet-Teller
CA	Carbon aerogel
CAF	Caffeine
CCA	Carrageenan derived carbon aerogel
DNA	Deoxyribonucleic acid
FTIR	Fourier-Transform Infrared
GG	Guar gum
GGCA	Guar gum derived carbon aerogel
HCl	Hydrochloric acid
<i>IR</i>	Impregnation ratio
IUPAC	International Union of Pure and Applied Chemistry
KBr	Potassium bromide
KG	Konjac gum
KGCA	Konjac gum derived carbon aerogel
KOH	Potassium hydroxide
NaOH	Sodium hydroxide
NaCl	Sodium chloride
Na ₂ CO ₃	Sodium carbonate
MTF	Metformin
PCA	Pectin derived carbon aerogel
PCM	Paracetamol

PH	Psyllium husk
PHCA	Psyllium husk derived carbon aerogel
RF	Resorcinol formaldehyde
SACA	Sodium alginate derived carbon aerogel
SOCA	Sago derived carbon aerogel
SEM	Scanning electron microscopy
UV-Vis	Ultraviolet-visible
WHO	World health organization
XG	Xanthan gum
XGCA	Xanthan gum derived carbon aerogel
ZnCl ₂	Zinc chloride

LIST OF SYMBOLS

λ	Wavelength
ε	Absorption coefficient
A	Temkin isotherm constant
Abs	Absorbance
A_T	Temkin equilibrium binding constant
a	Initial adsorption rate
B	Temkin isotherm constant
b	Langmuir isotherm constant
b_T	Temkin constant related to sorption heat
C_{Ae}	Concentration
C_e	Equilibrium concentration
C_0	Initial concentration
C_t	Concentration at time, t
K_d	Adsorption coefficient
K_F	Freundlich isotherm constant
K_L	Langmuir isotherm constant
k_1	Pseudo-first-order kinetic rate constant
k_2	Pseudo-second-order kinetic rate constant
M	Mass of adsorbent
N	Total number of data points
n	Adsorption intensity related to Freundlich constant
$^{\circ}C$	Degree celsius
pK_a	Acid dissociation constant

pH_{initial}	Initial pH
pH_{final}	Final pH
pH_{ZPC}	Point of zero charge
Q_0	Monolayer adsorption capacity
q_e	Adsorption equilibrium uptake
q_t	Adsorption uptake at time, t
q_{cal}	Calculated adsorption capacity
q_{exp}	Experimental adsorption capacity
$q_{e,\text{calc}}$	Calculated solution concentration at equilibrium
$q_{e,\text{meas}}$	Measured solution concentration at equilibrium
R	Universal gas constant
R^2	Determination of coefficient
T	Transmittance
t	Reaction time
V	Solution volume
V_T	Total pore volume
ΔG°	Gibbs free energy change
ΔH°	Enthalpy change
ΔS°	Entropy change
Δq	Normalized standard equation
$1/n$	Heterogeneity factor

**PEMBANGUNAN KARBON AEROGEL BERASASKAN POLISAKARIDA
UNTUK PEMULIHAN AIR TERCEMAR FARMASEUTIKAL**

ABSTRAK

Penyediaan karbon aerogel mesra alam melalui pengeringan tekanan atmosfera berasaskan polisakarida semulajadi terutamanya carrageenan, pektin, sagu, gum guar, gum konjac, gum xanthan, sekam psyllium dan natrium alginat telah dikaji. Prestasi untuk perawatan kompaun farmaseutikal, paracetamol (PCM), metformin (MTF), amoksisilin (AMX) dan kafein (CAF) telah diperiksa. Keadaan penyediaan telah dioptima dari segi kesan ejen pengaktifan, nisbah impregnasi (*IR*), suhu pengaktifan dan masa pengaktifan. Morfologi permukaan menunjukkan struktur poros 3D yang baik dengan luas permukaan spesifik antara 729.34 m²/g hingga 2165.94 m²/g. Penjerapan meningkat mengikut kecerunan konsentrasi yang meningkat. Penjerapan MTF, AMX dan CAF sangat bergantung pada perubahan pH larutan. Data keseimbangan sesuai dipadankan dengan model isoterma Langmuir, Freundlich dan Temkin dengan kapasiti penjerapan maksimum 416.79, 329.80, 583.11 dan 324.90 mg/g., bagi PCM, MTF, AMX dan CAF masing-masing. Kinetik penjerapan mematuhi model kinetik urutan pseudo-kedua dan parameter termodinamik menunjukkan sifat spontan, ciri endotermik dan eksotermik interaksi penjerapan. Penyelidikan ini telah berjaya menerokai penyediaan alternatif karbon aerogel semulajadi untuk perawatan kompaun farmaseutikal, khususnya PCM, MTF, AMX dan CAF dalam sumber air.

**DEVELOPMENT OF POLYSACCHARIDE DERIVED CARBON
AEROGELS FOR THE REMEDIATION OF PHARMACEUTICALS
CONTAMINATED WATER**

ABSTRACT

The preparation of eco-friendly carbon aerogels via ambient pressure drying using natural polysaccharides, mainly carrageenan, pectin, sago, guar gum, konjac gum, xanthan gum, psyllium husk and sodium alginate have been conducted. The adsorption performance for the remediation of pharmaceutical compounds, namely paracetamol (PCM), metformin (MTF), amoxicillin (AMX) and caffeine (CAF) has been examined. The preparation conditions were optimized, particularly the effects of activation agent, impregnation ratio (*IR*), activation temperature and activation time. Surface morphology projected well developed 3D porous structure of the carbon aerogels, with the specific surface area ranging between 729.34 m²/g to 2165.94 m²/g. The adsorptive uptakes increased proportional to the rising concentration gradients. The adsorption behaviour of MTF, AMX and CAF were highly dependent on the changing solution pH. The equilibrium data were described by the Langmuir, Freundlich and Temkin isotherm model, with maximum adsorption capacity for PCM, MTF, AMX and CAF of 416.79, 329.80, 583.11 and 324.90 mg/g, respectively. The adsorption kinetics were best fitted to the pseudo-second order kinetic model and thermodynamic parameters revealed the spontaneity, endothermic and exothermic characteristics of the adsorption interaction. This research has successfully explored an alternative pathway for preparation of natural carbon aerogels for the possible treatment of pharmaceutical compounds, specifically PCM, MTF, AMX and CAF from aqueous solution.

CHAPTER ONE

INTRODUCTION

1.1 An overview of the current development and applications of carbon aerogels

Carbon aerogels are extraordinary material, due to their exceptional properties, with high specific surface area, wide porosity, low density, coupled with the flexible synthesis methods. The fascinating development of carbon aerogel lies in the versatile synthesis step of the sol-gel technique, the possibilities of a variety of raw precursors, and the diverse activation methods to design and tailor the chemistry of different carbon aerogels. The estimated world-wide production of aerogel was reported at USD 115.7 million in 2011, and it was projected to increase up to USD 1376.6 million by 2017 (Smirnova and Gurikov, 2017).

The development of carbon aerogel is predicted to be continued in the next few decades, with synchronised improvement in the material features related to the corresponding manufacturing steps, which are the vital factors controlling the production costs (Maleki and Hüsing, 2018). Although the innovation on the specific characteristics of aerogels and the hybrid composites are highly desirable, a vast group of these aerogels are unsuitable for commercialization purpose, mainly attributed to the bad formability, low production yield and high manufacturing cost (Zuo *et al.*, 2015). These high specific surface area, excellent mechanical strength, and wide electrical conductivity and flexibility, would find wide applications for energy storage devices, water purification technology and remediation of emerging contaminants (Araby *et al.*, 2016).

1.2 Problem statement

For years, the development of carbon aerogels is still restricted for laboratory scale applications, contributed mainly by the high processing cost, initial raw precursors, extensive gelation time, toxic chemicals, and the complex synthesise process (Kumar *et al.*, 2016; Yu *et al.*, 2017). These carbon aerogels are synthesized by a sol-gel polymerization reaction of resorcinol and formaldehyde, subsequent by solvent exchange, supercritical drying and pyrolysis using inert gas. The special drying under supercritical or freeze conditions is considered as a necessary step to allow the formation of a porous structure. The major challenges of the preparation step has therefore enhanced the overall operation cost, besides raised the safety concern as it usually operates at a relative high pressure of exceeding 7.5 MPa (Oladunni *et al.*, 2018).

Another typical concern in the preparation of carbon aerogels involves the requirement of highly hazardous resorcinol and formaldehyde (RF), carbon containing fibers, graphene and carbon nanotube as the major raw precursors. The preparation step would produce carbon aerogels with poor mechanical strength, with the possible generation of secondary pollutions. Therefore, the pressing need of using natural biopolymers, notably polysaccharides, amino acid and proteins are predicted to be the excellent organic sources for the preparation of high quality carbon aerogel (Guilherme *et al.*, 2015). These renewable materials are defined as the “green gold” in the next generation of carbon aerogels. (Xiong *et al.*, 2018; Yang *et al.*, 2018).

This new group of functionalized adsorbents presents itself as an excellent candidate for the environmental remediation of the emerging gas and water pollutants (Yin *et al.*, 2016). Defined as the “chemical substances that are suspected to cause

adverse unknown effects to the human health and ecosystems”, pharmaceuticals are a major class of growing contaminants which has attracted huge interest among the scientific community due to the potential health risks and their interactions with the landscape, human beings and wildlife species (Deblonde *et al.*, 2015; Garcia-Ivars *et al.*, 2017). The molecular characteristics of pharmaceuticals, typically within the molecular mass of <500 Da, differentiate them from conventional industrial chemicals, mainly attributed to their ability to form chemically complex structures, polar molecules consisting of more than one ionisable groups, the flexibility to be transported from urban areas to rural areas and / or vice versa (Madikizela *et al.*, 2018).

A considerable amount of these pharmaceutical residuals have been systematically discharged into the aquatic environment, via municipal wastewater treatment plants, hospitals, pharmaceutical production facilities, aquaculture and agricultural settings (Bielen *et al.*, 2017; Hong *et al.*, 2018). Despite the low concentration of pharmaceutical drugs was detected in the waterways, their continuous input establishes an important ecological threat according to their persistence and hazardous characteristics (Álvarez-Torrellas *et al.*, 2018). In Malaysia, the detection of a series of pharmaceutical contaminants have been reported at Langat river and Tangkas river, Selangor (Al-Odaini *et al.*, 2010; Al-Qaim *et al.*, 2013), and at sewage treatment plants, hospitals and surface water in Negeri Sembilan (Al-Qaim *et al.*, 2014). Nevertheless, there are limited studies that have been conducted for the possible treatment of these pharmaceuticals release.

Within this framework, a wide range of treatment technologies have been implemented. However, the wide scale application of these technologies are hampered by the major drawbacks of complex treatment processes, high investment and maintenance cost, and generation of toxic sludge and by-products (Sophia and Lima,

2018). Among all, adsorption process is garnering much attention, due to its simple design, cost-effective operation, no generation of by-product, possibility of adsorbent regeneration, and capable of handling macro, meso or micro pollutants (Nielsen and Bandosz, 2016; Álvarez-Torrellas *et al.*, 2017). In this sense, the present work was conducted to engineer a wide range of eco-friendly, and natural carbon aerogels by using ambient pressure drying technique for the effective remediation of the new emerging pharmaceutical contaminants, mainly paracetamol, metformin, amoxicillin and caffeine.

1.3 Research objectives

The objectives of this work are:

- (a) To prepare and characterize a series of polysaccharide derived carbon aerogels using ambient pressure drying technique
- (b) To optimize the operational parameters for the preparation of carbon aerogels.
- (c) To examine the performance for the adsorptive remediation of pharmaceutical contaminated water.
- (d) To evaluate the isotherm modelling and kinetic of the adsorption process.
- (e) To determine the thermodynamic analysis of the treatment system.

1.4 Scope of study

This study evaluated the preparation of the highly porous carbon aerogels, from polysaccharide via ambient pressure drying. The effects of activation agent, chemical impregnation ratio, activation temperature, and activation time to adsorptive uptakes

of different pharmaceuticals were evaluated. The prepared adsorbents were featured using Scanning Electron Microscope (SEM), Fourier Transform infrared spectroscopy (FTIR), nitrogen adsorption-desorption analyzer and zeta potential measurement (pH_{ZPC}) for the evaluation of surface morphology, functional characteristics, pore properties and surface charge.

The batch adsorption experiments were conducted for the adsorptive uptake of paracetamol, metformin, amoxicillin and caffeine, with respect to the changing initial concentrations, contact time and solution pH. The equilibrium data were fitted to the non-linear Langmuir, Freundlich and Temkin isotherm models, while the kinetic analysis were simulated using the pseudo-first-order, pseudo-second-order and Elovich kinetic equations. Thermodynamic evaluation, notably Gibbs free energy, enthalpy and entropy change were outlined.

1.5 Significance of study

Over the past few decades, pharmaceutical consumption has increased tremendously with more than 3000 active substance available commercially and new compounds are continuously introduced in the market, mainly ascribed to the advances of health care and research development, world population growth and rising life expectancy (Silva *et al.*, 2018). As a result, pharmaceuticals have been detected in sewage effluents, surface water, ground water and in drinking water at trace levels. Current water treatment technology and techniques could not serve as the complete barriers against these pharmaceuticals. These persistent compounds present a long term risk to aquatic organisms due to the continual input into the aquatic environment,

and its removal prior reaching to the receiving waters is absolutely imperative to avoid potential risks to the ecosystem.

Accordingly, this research focused on the remediation of the frequently used pharmaceutical contaminants, mainly paracetamol, metformin, amoxicillin and caffeine using polysaccharide derived carbon aerogels, a new class of material associated with an extensive variety of applications. The novel development of the polysaccharide derived carbon aerogels is an innovative proposition to remove the pharmaceuticals pollutants, that has been established in the waterways in Malaysia. The usage of benign raw precursors that are renewable, abundant, and non-toxic to substitute man-made polymers as raw materials, could minimize the environmental and health implications associated with the conventionally prepared carbon aerogels.

Compared to the conventional supercritical drying method which is energy intensive and dangerous, the proposed ambient pressure drying process suggested an economical and technically scalable route to acquire superior carbon aerogels, while the application of natural polysaccharide appears to be an excellent alternative to the commonly applied resorcinol and formaldehyde (Bakierska *et al.*, 2014; Singh *et al.*, 2016). The novel application for the treatment of the pharmaceuticals, widely detected in sewage effluents, surface waters, ground waters and in drinking water, has prevailed to be a breakthrough in solving the new alarming pollution concern among the scientific community, for the sustainability of the future generations.

1.6 Organisation of the thesis

This thesis contains five major chapters, with Chapter 1 provides a brief introduction on the carbon aerogel development and applications. The problem

statement, research objectives, scope and the significance of the research were highlighted.

Chapter 2 summarizes, the definition, specific features and history of carbon aerogels. The preparation procedures, operating parameters, adsorptive capability, and the respective limitations were outlined. The pharmaceutical pollutants, pertaining to their classification, usage, environmental and health implications, and the current treatment systems were elucidated. Chapter 3 describes the details of chemicals, reagents, and materials applied in this research. The experimental procedures including the preparation method, optimization studies, characterizations and performance analysis were discussed.

Chapter 4 presents the results and discussions of the research findings. The effects of preparation parameters, performance analysis related to the operating conditions, mainly the effect of activation agent, chemical impregnation ratio, activation temperature, and activation time were highlighted. The adsorption equilibrium, kinetic and thermodynamic evaluation of the adsorption system, together with the physical, chemical and physiochemical characterizations were elucidated. The conclusions of this research were given in Chapter 5, while the recommendations for the future studies were listed.

CHAPTER TWO

LITERATURE REVIEW

Chapter two presents the comprehensive literature study related to the specific features of carbon aerogel, its evolution, distinctive properties and novel applications. The preparation procedure, notably the sol-gel method, aging, drying, carbonization and activation step are highlighted. The detailed description of the natural polysaccharide, pharmaceutical compounds, notably paracetamol (PCM), metformin (MTF), amoxicillin (AMX) and caffeine (CAF) are highlighted. Additionally, fundamental importance of the adsorption process, controlling parameters, isotherm, kinetic models and thermodynamic analysis are elucidated.

2.1 Carbon aerogel

2.1.1 Definition and evolution

The international union of pure and applied chemistry (IUPAC) defined aerogel as a “gel comprised of a microporous solid in which the dispersed phase is a gas” (McNaught and Wilkinson, 1997). To clarify, aerogel is a conventional terminology refers to any material, derived from organic, inorganic or hybrid molecular precursors, that is generally prepared via sol-gel process, accompanied by a suitable drying technique, in which the three-dimensional and highly porous network structure of the gel is preserved (Maleki and Hüsing, 2018). Aerogels are porous solid materials constructed of colloidal or polymer particles that exhibits high surface area (500-1000 m²/g), low bulk density (0.003–0.15 kg/m³), electric resistivity and high porosity (80-99.8 %) (Chen *et al.*, 2014; Smirnova and Gurikov, 2017). Aerogel was firstly

discovered by Kistler in 1930's when the liquid portion from a gel was removed, while compromising the volume of the original wet gel, via supercritical drying. Meanwhile in late the 1980's, Pekala introduced the existing organic aerogel synthesized from resorcinol-formaldehyde which provided a more porous network (Pekala and Kong, 1989). Since the first introduction by Pekala and co-workers, significant research efforts has been undertaken to develop carbon aerogels, and the growth arose owing to advances in precursor chemistry and the drying technique. A summary of the historical development of aerogels is stipulated in Table 2.1.

Owning different capabilities and uniqueness, aerogels have been classified into various forms, and distinguished either by their composition or preparation method. White *et al.* (2014) have defined the classification of aerogel according to its composition: organic, inorganic and metallic, while Du *et al.* (2013) have distinguished it according to the component of formation: single component and aerogel composites, as depicted in Figure 2.1. The initial growth of aerogel research focused mainly on the compositions, mainly silica, non-silica oxides, resorcinol formaldehyde (RF) aerogels, carbon aerogels (mainly carbonized RF aerogels) and aerogel composites, and lately expanded into inorganic (Pinheiro *et al.*, 2017), organic (Chaisuwan *et al.*, 2010), polymethylsilsesquioxane (Lin and Hsu, 2017), carbon nanotubes (Dong *et al.*, 2015), graphene (Zhou *et al.*, 2018) polysaccharide (Groult and Budtova, 2018), starch (Ubeyitogullari and Ciftci, 2016), composite (Dou *et al.*, 2011), and graphene-silicon carbide (Jiang *et al.*, 2018).

Table 2.1: Historical evolution of aerogels

Year	Development	References
1931	Aerogel discovery by Samuel Stephens Kistler.	Kistler (1931)
1932	Synthesis of stannic oxide, alumina, tungstic oxide, nickel tartarate, nitrocellulose, gelatin, cellulose, egg albumin and agar aerogels.	Kistler (1932)
1950	The first silica aerogel was produced by Mosanto, under the tradename Santocel®, using supercritical alcohol extraction, adapted from Kistler.	Smith <i>et al.</i> (1995)
1976	Development of SiO ₂ , MgO, TiO ₂ , Al ₂ O ₃ , ZrO ₂ and mixed oxides aerogels.	Teichner <i>et al.</i> (1976)
1980's	Supercritical CO ₂ was proposed as a new drying scheme for silica aerogels to substitute alcohol in alcogel. Tetramethyl orthosilicate (TMOS) was substituted with tetraethyl orthosilicate (TEOS) due to its high toxicity.	Tewari <i>et al.</i> (1985); Tewari and Hunt (1986)
1985	The first “International symposiums of aerogels” was held in Germany	Fricke (1988)
1989	Development of organic aerogel from resorcinol-formaldehyde at the Lawrence Livermore National Laboratory in Berkeley. The heating method was discovered.	Pekala and Kong (1989)
1991	An ultralow density silica aerogel at 3.1 mg/cm ³ was developed by Dr. Tillotson at the Lawrence Livermore National Laboratory, to break the Guinness world record as the lowest density solid.	Tillotson and Hrubesh (1998)

Table 2.1: Continued

Year	Development	References
1996	A novel route for preparation of high surface area was developed by carbon dioxide assisted activation.	Hanzawa <i>et al.</i> (1998)
2007	Carbon nanotube aerogel was prepared by dissolving carbon nanotube with surfactant, subsequent by ion sonicated, gelled, dried and further improved with polyvinyl alcohol.	Bryning <i>et al.</i> (2007)
2009	Graphene aerogel was obtained from transforming graphene oxide solution using ultrasonic gelation method, drying and thermal reduction.	Wang and Ellsworth (2009)
2011	Carbon aerogel (resorcinol formaldehyde) was crystallized into diamond aerogel by a laser heated diamond anvil cell using high temperature and pressure.	Pauzauskie <i>et al.</i> (2011)
2012	Development of polymerized aerogel “polyimide aerogel” at Nasa’s Glenn research centre.	Meador <i>et al.</i> (2008)

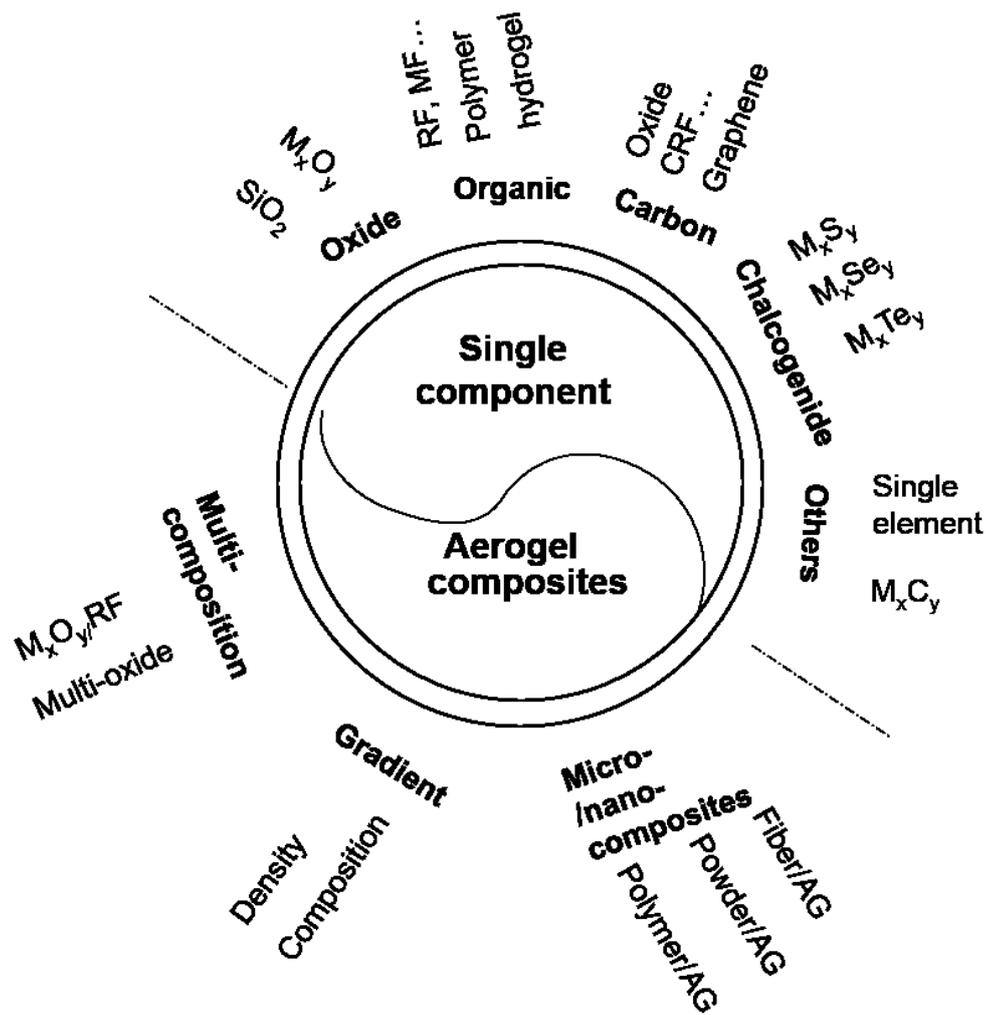


Figure 2.1: The classifications of aerogel (Du *et al.*, 2013)

2.1.2 Specific features of carbon aerogel

Carbon aerogel is the latest edition of carbonaceous materials, that has rapidly grown, due to its outstanding features including high porosity, ultralight, large specific surface area, low thermal conductivity and density. The idea of carbon aerogels were firstly established by Pekala and his colleagues in 1980s. The properties of carbon aerogel can be tailor-made by the adjustments of different synthesis conditions, composition, sol-gel concentrations, type of catalysts, drying process and

carbonization temperature (Singh *et al.*, 2016). The tuneable porous structures allows carbon aerogels to be applied for highly versatile applications, specifically catalyst support, catalysis, adsorbents, supercapacitors, insulators, hydrogen storage and drug delivery system (Zhang *et al.*, 2018). The additional advantage of carbon aerogel is the additional properties to be reproduced in the form of monoliths, beads, powders or thin films. Nonetheless, the specific application of carbon aerogel is not confined only by the porosity structure, as the surface chemistry is another important factor to affect the overall performance (Wang *et al.*, 2018).

The traditional carbon aerogel is fabricated by the carbonization of organic aerogels, mainly resorcinol formaldehyde aerogel. The preparation method comprises of sol-gel synthesis, aging, solvent exchange, drying and high temperature carbonization. However, the requirement of these costly and hazardous precursors, lengthy preparation procedure, and energy intense process have hampered the large scale production and supply of carbon aerogels, that would introduce harmful substances to the surrounding environment, with the formation of toxic by-products (Xu *et al.*, 2018).

2.1.3 Distinctive properties and applications of carbon aerogel

2.1.3(a) Electrochemical

Carbon aerogels are the earliest electrically conductive aerogels with fascinating characteristics, notable electro-conductivity (approximately 100 S/cm), large surface area (up to 1100 m²/g), high current density, polarizability, wide porosity and non-participation in faradaic reaction, making it an appropriate representative for high performance electrochemical applications (Allahbakhsh and Bahramian, 2015).

Carbon aerogel nanospheres embedded in ultrathin transition metal selenides was reported to acquire good electro conductivity and outstanding structure stability and remarkable performance as bio sensing platform towards 17β -estradiol. The carbon aerogel prepared via hydrothermal strategy displayed promising potential in energy storage and electrochemical sensing (He, 2017). Wang *et al.* (2018) fabricated macro-meso-microporous carbon aerogel, with specific surface area of $1811 \text{ m}^2/\text{g}$ via carbonization of alginate aerogel at $800 \text{ }^\circ\text{C}$, that projected excellent electrochemical performance in supercapacitors. Oxidation modified carbon aerogels were synthesized via Hummers oxidation method to improve the properties of the carbon aerogel, with the specific surface area at $450 \text{ m}^2/\text{g}$, and specific capacitance of 151 F/g at 0.5 A/g . The oxidation-modified method produced high surface area and specific capacitance, good rate capability and cycling performance of carbon aerogel, which delivered a promising material for the preparation of supercapacitors and batteries (Xu *et al.*, 2018). Conversely, the synthesis of bamboo cellulose fibers derived carbon aerogel was subjected to sol-gel process, freeze dried at $-85 \text{ }^\circ\text{C}$, and carbonized between 700 to $1000 \text{ }^\circ\text{C}$ using potassium hydroxide activation to obtain supercapacitor with surface area of $910 \text{ m}^2/\text{g}$, and specific capacitance of 381 F/g (Yang *et al.*, 2018).

2.1.3(b) Catalyst

One of the utmost applications for carbon aerogels and their derivatives is the catalyst systems. The ability to synthesize carbon aerogels into various forms (beads, powders) and the physicochemical surface properties of metal doped carbon aerogels mark them as promising materials for catalysis application (Araby *et al.*, 2016). Hu *et al.* (2016) investigated the feasibility of dye regeneration by the catalytic oxidation of

mesoporous carbon aerogel supported cobalt oxide nanoparticles. The waste effluent which undergone catalytic ozonation was successfully to be reused twice. Perovskite-carbon aerogel composites with 3D porous structure which was applied as a heterogeneous catalyst in a microwave assisted catalytic degradation of fuchsin basic dye, has accomplished the complete degradation within 6 minutes. The catalytic degradation efficiency could remain at approximately 94% even after five cycles (Wang *et al.*, 2018c). The catalytic activity of cobalt-doped carbon aerogel was evaluated by Hu *et al.* (2017) for the activation of peroxymonosulfate for the removal of organic contaminants. The monolithic carbon aerogel was synthesized by resorcinol-formaldehyde resin and co-condensation of graphene oxide, in the presence of cobalt ions. The aerogels were lyophilized, carbonized and thermal treated in air. The catalyst possessed large surface area of 670 m²/g, and remains operational in practical application as compared to traditional powder catalysts.

2.1.3(c) Thermal insulator

The low thermal conductivity, unique nanostructure, high porosity, lightweight and nanoporous structures of carbon aerogels has received great specific interest as the thermal insulation material for buildings (Zuo *et al.*, 2015). These highly porous carbon aerogels were synthesized via sol-gel polymerization, carbonization at 800 °C, and carbothermal reduction at 1500 °C of novolac-silica aerogels. The prepared composite aerogel projected high porosity of > 82% and low density of < 0.3 g/cm³, which is suitable for thermal insulation systems (Seraji *et al.*, 2015). An important feature of carbon aerogel required for thermal insulation is monolithicity, however, this is hampered by the fragility and brittleness associated with complicated carbon

aerogel processing method. To overcome this disadvantage, Jia *et al.*, (2016) have synthesized low density and mechanically robust carbon aerogel monoliths via ambient pressure drying of phenolic resin and hexamethylenetetramine. The carbon aerogel monoliths exhibited low density up to 0.07 g/cm^3 , high mechanical strength of 0.9-5.0 MPa and low thermal conductivity (0.032-0.069 W/m K), which can be fabricated into various shapes for high temperature insulators. Similarly, in an effort to overcome the brittleness of carbon aerogel for thermal insulation, carbon fiber reinforced composites were synthesized by copolyolysis of polyacrylonitrile fiber reinforced organic aerogel composites via supercritical drying. The resulting composite exhibited crack-free material with the thermal conductivity of 0.073 W/m K, which may lead to large scale process (Feng *et al.*, 2012).

2.1.3(d) Hydrogen storage

Porous materials have become an attractive option for hydrogen storage as they are light weight, demonstrate rapid kinetics, reversible, with controllable pressure of adsorption and desorption of hydrogen. Platinum doped carbon aerogel via ambient pressure drying with submicropore size (0.3-1.46 nm) is beneficial for hydrogen storage, with great reversibility at room and liquid nitrogen temperature conditions (Singh *et al.*, 2016). Carbon aerogels confined with magnesium nanoparticles were successfully prepared via hydrogenation of dibutyl-magnesium, subsequent by hydrogen desorption at 623 K, with an apparent activation energy of 29.4 kJ/mole H_2 . The composite with the specific surface area of $1267.1 \text{ m}^2/\text{g}$ and an average pore size of 19.0 nm is a promising hydrogen storage material (Liu *et al.*, 2013). Similarly, Robertson and Mokaya (2013) have successfully synthesized microporous carbon

aerogels via subcritical drying and KOH activation, with the resultant surface area between 915-1980 m²/g, pore volume of up to 2.03 cm³/g and pore size between 8 and 13 Å. The activated carbon aerogels exhibited high hydrogen storage capacity between 3.5 and 4.3 wt% at 196 °C and 20 bar.

2.1.3(e) Adsorption

Carbon aerogel with the large surface area, light weight and highly porous is an excellent candidate for the remediation of environmental pollutants. An eco-friendly carbon aerogel synthesized via carbonization of sodium carboxymethyl cellulose aerogels, and treated via KOH activation process exhibited high specific surface area of 428 m²/g. The aerogel projected an excellent adsorption uptake of methylene blue and malachite green dyes of up to 249.6 and 245.3 mg/g, respectively (Yu *et al.*, 2017). The preparation of an inexpensive carbon fibre aerogel using natural bamboo fibre via carbonization was reported by Jiao *et al.*, (2016). This super hydrophobic adsorbent exhibited the adsorption efficiency of different organic liquids of up to 23 – 51 times the weight of the adsorbent. The lightweight adsorbent also showed excellent recyclability and provided new insights into the renewable utilization of low cost biomass resources. The application of graphite natural rocks for the synthesis of graphene-carbon nanotube aerogels were reported by Kabiri *et al.* (2014). The high specific surface area of the adsorbent at 315 m²/g, exhibited outstanding performance of the adsorption of petroleum products, organic solvents, fats, and 28 L adsorption uptake of oil per gram of adsorbent. The potential transformation of carbon aerogels into a commercially viable process is still in the development stage, and the available application of carbon aerogels are given in Table 2.2. The simple and economical production of carbon aerogel is highly scalable for water purification and

oil spill clean-up. The adsorptive capabilities of carbon aerogels for different water pollutants are given in Table 2.3.

Table 2.2: Available applications of carbon aerogel

Applications	Specific properties	Reference
Hydrogen storage	Excellent electrical conductivity, large specific surface area	Calvo, <i>et al.</i> (2009); Tian <i>et al.</i> (2010); Singh <i>et al.</i> (2016)
Catalysis	High mesoporosity, large specific surface area, phase stability	Moreno-Castilla and Maldonado-Hódar, (2005); Shao <i>et al.</i> (2013); Maleki and Hüsing (2018)
Adsorption	High porosity, large specific surface area, versatility, low bulk density, surface functionalization	Jiao <i>et al.</i> (2016); Yin <i>et al.</i> (2016)
Capacitive deionization	Appropriate pore structure and high specific surface area, conductivity, and wettability	Oladunni <i>et al.</i> (2018)
Absorption	High porosity and hydrophobicity	Li <i>et al.</i> (2014b)
Membrane/separation technology	High hydrophobicity and selectivity	White <i>et al.</i> (2014)
Flame retardant	Great mechanical properties and flammability with incorporation into polymeric aerogels	Zuo <i>et al.</i> (2015)
Sensor	High specific surface area and pore diameter, and surface functionalization	Dolai <i>et al.</i> (2017)

Table 2.3: Adsorption capability of carbon aerogels for different water pollutants

Classification	Precursor	Adsorbate	Adsorption uptake (mg/g)	References
Dyes	Starch	Crystal violet, methyl violet, methylene blue	1181-1515	Chang <i>et al.</i> (2010)
	Graphene / carbon sphere / silver	Methylene blue	66	Dubey <i>et al.</i> (2014)
	Sodium carboxymethyl cellulose	Methylene blue, malachite green	245- 250	Yu <i>et al.</i> (2017)
	Resorcinol/ furfural	Basic blue, acid red	360, 2650	Ling <i>et al.</i> (2011)
	Phenol / formaldehyde	Rhodamine B	95	Lin and Liang (2016)
Heavy metals	Resorcinol/ formaldehyde	Lead, mercury, cadmium	2-12	Kadirvelu <i>et al.</i> (2008)
	Graphene	Gold	104×10^{-5}	Kondratowicz <i>et al.</i> (2017)
	Geothite / graphene oxide / carbon nanotube	Arsenic compound	24-102	Fu <i>et al.</i> (2017)
	Waste paper/ chitosan	Copper	156	Li <i>et al.</i> (2018)
	Graphene oxide	Chromium	408	Liang <i>et al.</i> (2018)

Table 2.3: Continued

Classification	Precursor	Adsorbate	Adsorption uptake (mg/g)	References
Organic compounds	Resorcinol/ formaldehyde	Toulene	456	Maldonado-Hódar <i>et al.</i> (2007)
	Carbon-silica composite	Benzene	395	Dou <i>et al.</i> (2011)
	Bamboo fibre	Benzene, ethly acetate, chloroform, acetylyacetone, dimethylformamide, tetrachlorometane	23000 - 51000	Jiao <i>et al.</i> (2016)

2.2 Carbon aerogel preparation procedure

Generally, there are four major steps for the preparation of carbon aerogels: (1) sol-gel process (monomer compound, concentration, pH); (2) aging; (3) activation (temperature, time, activation ratio); (4) drying (supercritical, freeze drying or ambient pressure drying) and (5) carbonization and /or activation (Maldonado-Hódar, 2013). The preparation method for aerogel is a selective process which dictates the type of aerogel produced. A general preparation procedure for the carbon aerogels is depicted in Figure 2.2.

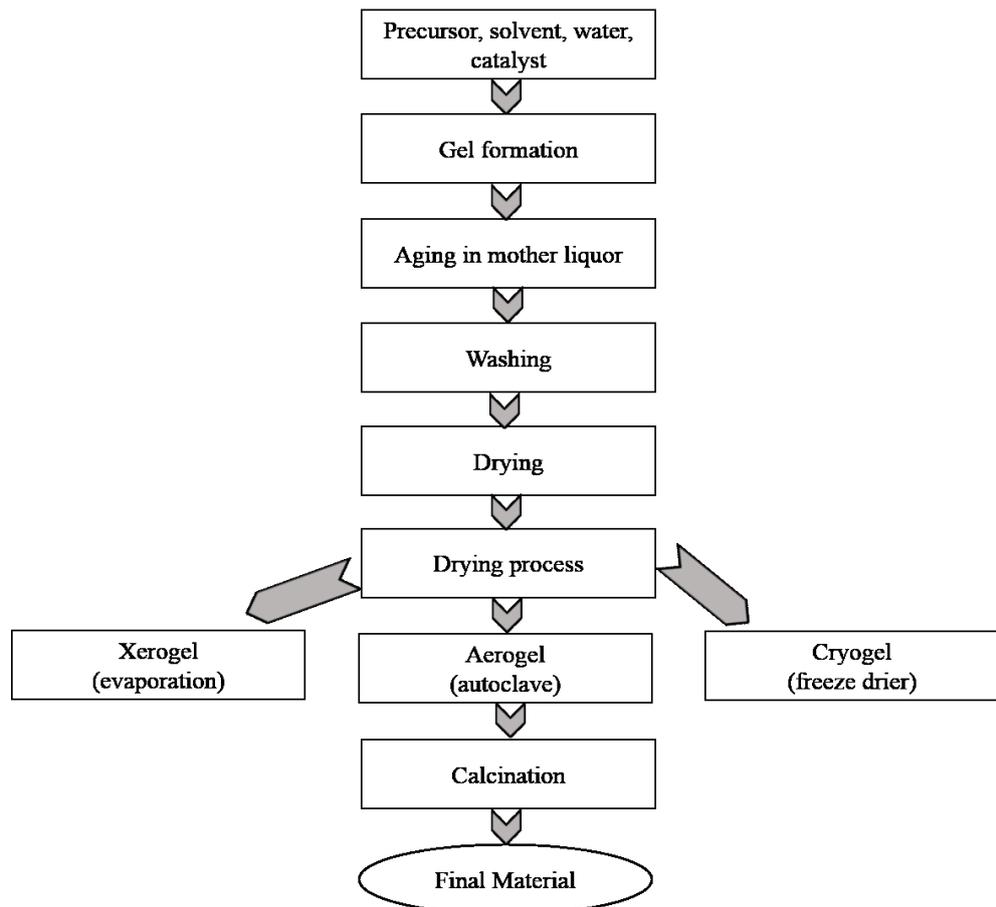


Figure 2.2: General procedure for the preparation of carbon aerogels (Pierre and Pajonk, 2002)

2.2.1 Sol-gel process

The most conventional and flexible method reported for the preparation of carbon aerogel is the sol-gel process, which is generally carried out in liquid solution at low temperature ($< 100\text{ }^{\circ}\text{C}$). Sol is defined as the suspension of colloids (diameter range: 1-100 nm), where else gel is defined as the stiff, extremely interconnected network comprised of continuous polymeric chains of micrometrics immersed in liquid (Baino *et al.*, 2018). The process is described by the transition of colloidal solution into a continuous network to the infiltrated fluid. A sol-gel reaction is a synthesis process that transforms a molecular precursor to a colloidal solution (sol), to acquire a solid material (gel) with the assistance of a chemical agent (crosslinker) or a physical intervention (changing the pH or temperature). The sol-gel process presents numerous advantages such as structural and chemical homogeneity, material purity, and dictates the resulting porosity of the material and the desired form of monolith, fibers, films or monosized powder (White *et al.*, 2014). Carbon aerogels are generally synthesized by the carbonization of dried polymeric materials derived from carbon or carbonaceous sol-gel reactions.

Figure 2.3 shows the schematic diagram of the sol-gel process of organic, bio based and carbonaceous materials, which represents the classic monomers for the development of carbon aerogels (Maleki and Hüsing, 2018). In general, resorcinol and formaldehyde are the most comprehensively applied carbon aerogel precursors, which could readily dissolve in water with the presence of a basic or acidic catalyst (Araby *et al.*, 2016). Recently, biomaterials as the molecular precursors have provided a promising alternative source in establishing physical interactions between the polymeric chain of the precursors by changing the physical or chemical conditions

(García-González *et al.* 2011). This 3D colloidal network is known as aquagel or hydrogel that could be transformed into highly porous carbonaceous aerogels.

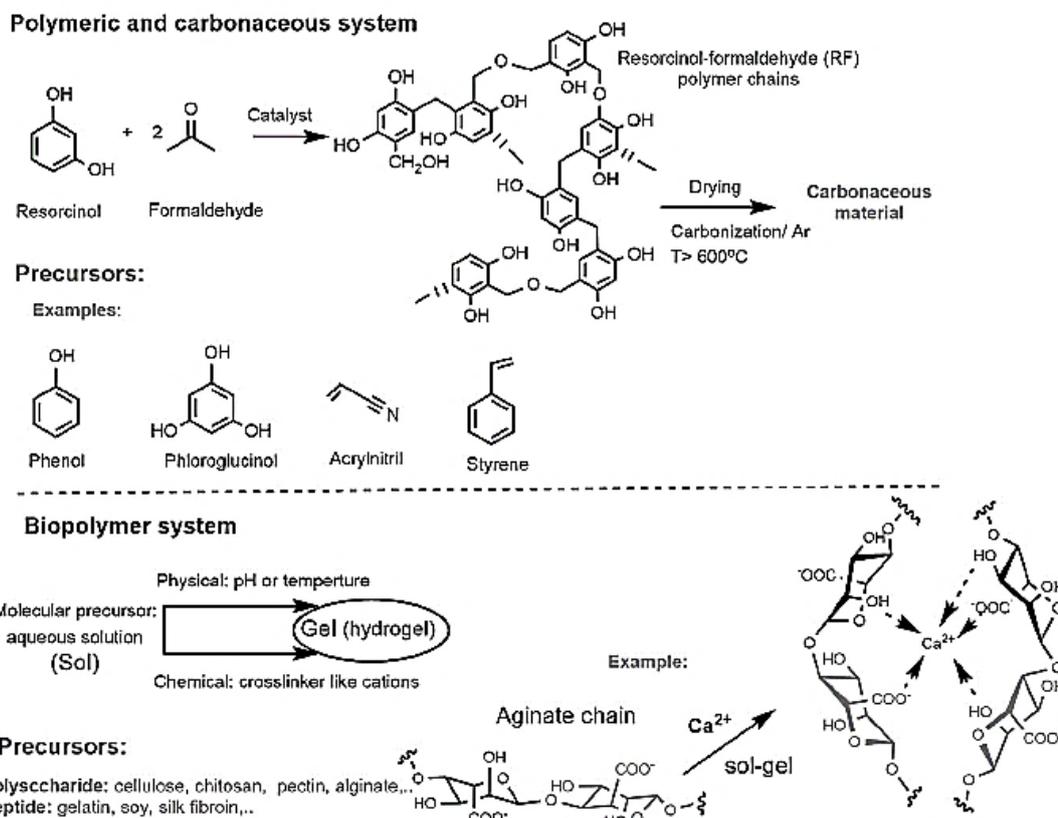


Figure 2.3: Representation of the sol-gel process

2.2.2 Aging

The wet-gel obtained from the sol-gel process is subjected to aging process, to ensure all the precursors are consumed and to mechanically strengthen the weak solid skeleton formed through the sol-gel process. During the aging process, polycondensation of the wet-gel begins, which increases the strength of the material matrix and decreases the porosity of the material to avoid cracking (Chang *et al.*, 2010). The colloidal network formed would be left to advance in the mother liquor by controlling the temperature, time and pH, which would remarkably impact the physical properties

through Ostwald ripening, sintering and syneresis phenomena (Brinker and Scherer, 2013). The changing physical properties of the gel after the aging stage is irreversible.

2.2.3 Drying

The drying step is the key factor for the preparation of carbon aerogels. In the drying step, the pore filling liquid in the aged gels, either water or alcohol is usually removed via supercritical drying, freeze drying, ambient pressure drying, vacuum drying and microwave drying. Evaporation of wet gel would lead to the collapse of the capillary pressure that builds up in the pore walls, created by the surface tension of the liquid (Vareda *et al.*, 2018). Consequently, supercritical drying technique was introduced for the preparation of low density aerogel, and to avoid the collapse of the pore structure. However, the supercritical drying is a time consuming process, that requires multistep technique and unreliable for large scale production (Guo *et al.*, 2016). Lately, ambient pressure drying is depicted to be a suitable technique for large scale production of carbon aerogels, due to its simplicity and energy saving route. This method produces low density monoliths, causes shrinkage, and may establish a low porous solid. In view of the shortcomings of the drying method, ambient pressure drying method was upgraded by the introduction of activation agents to reduce capillary drying stress (Land *et al.*, 2001). The advantages and the disadvantages of the generally used carbon aerogel drying techniques are given in Table 2.4 (Calvo *et al.*, 2011).