# CHAPTER II LITERATURE REVIEW

### 2.1 CO<sub>2</sub> Capture

 $CO_2$  from human activities are the major sources for green house gases that cause global warming.  $CO_2$  is much less atmospheric damaging than methane, a hydrocarbon gas nevertheless, it is essential to take urgent steps to reduce  $CO_2$ emissions because it has high amount in the atmosphere.

The largest source to the emission of  $CO_2$  is the energy sector, which includes combustion of fossil fuels like oil, coal and natural gas, and other processes/systems, such as coal-fired power plants, cements manufacturing plants, refineries, transportation etc. as shown in Figure 2.1

CO<sub>2</sub> separation processes (Figure 2.2 and Table 2.1) can be pre-combustion, post-combustion, and oxy-combustion, (Thiruvenkatachari *et al.*, 2009).

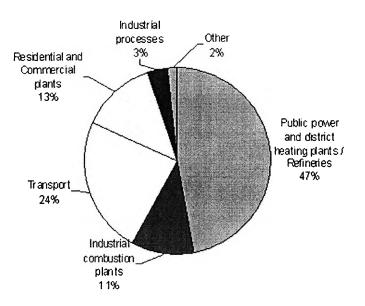
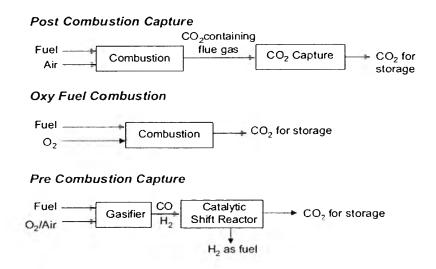


Figure 2.1 Emissions of CO<sub>2</sub> (National Environmental Research Institute, 2004).

Post combustion  $CO_2$  capture is a process where the  $CO_2$  is separated or removed from a flue gas containing  $CO_2$  mixed with other gasses. The purpose of the process is to get a gas of pure  $CO_2$  that can be safely stored. In 2002, Moore *et.al.* developed and demonstrated a solid oxide fuel cell (SOFC) to enable adsorption of carbon dioxide. Post combustion processes are developed with the lowest cost and consume significant amount of energy for regeneration of the absorption solvent when compare to other method. In SOFC, the driving force for the oxygen separation is the oxidation reaction without expenditure of additional energy.

Pre-combustion  $CO_2$  capture is a process where the carbon in the fuel is separated or removed before the combustion process. Instead of burning coal or natural gas in a combustion plant, fuel can be converted to hydrogen and  $CO_2$  prior to combustion. The  $CO_2$  can then be captured and stored, while the hydrogen is combusted to produce power.

Oxyfuel combustion with  $CO_2$  capture is very similar to post-combustion  $CO_2$  capture. The main difference is that the combustion is carried out with pure oxygen instead of air. As a result, the flue gas contains mainly  $CO_2$  and water vapor, which can be easily separated. The challenge is that it is expensive to produce pure oxygen. (http://www.bellona.org/ccs/Artikler)



**Figure 2.2** Three different pathway of the  $CO_2$  separation processes (Thiruvenkatachari *et al.*, 2009).

Technologies	Current status	Pros	Cons
Post-	- Amine scrubbing is	Existing Technology	Energy penalty
combustion	well established for	Retrofit to existing	due to solvent
capture	natural gas	power-plant designs	regeneration.
	- Solvent degradation	Extra removal of	Loss of solvent
	is a problem	$NO_x$ and $So_x$	
	- Some small power		
	plants Operating.		
Pre-	- Integrated	Existing Technology	Cooling of gas
combustion	gasification combined	Very low emissions	to capture $CO_2$
capture	cycle (IGCC) and		is necessary.
	ammonia production		Efficiency loss
	are well established		in water gas
	- Physical solvent		shift section
	separation is well		
	established		
	- Gas turbines must be		4
	capable of using		
	H <sub>2</sub> -rich fuel.		
Oxyfuel	- Oxygen production	Existing Technology	High energy
combustion	is well established	Absence of nitrogen	input for air
	- Small scale	eliminates NO <sub>x</sub>	separation.
	combustor test rigs	emissions. Absence of	Combustion in
	operating.	nitrogen provides low	pure oxygen is
		volume of gases and	complicated
		so reduced size of	
		entire process	

 Table 2.1
 Current status of CO2 capture technologies (Olajire, 2010)

### 2.1.1 CO<sub>2</sub> Capture Technologies

There are many technologies developed in decades for carbon dioxide capturing from the combustion/gasification system to reduce the greenhouse gas problem. It can be characterized as liquid solvent based technologies, solid adsorbent based technologies, membrane separators, and low temperature systems. The detail and limitation of the technologies in each area are discussed.

### 2.1.1.1 Liquid Solvent Based Technologies

These technologies used either a chemical or a physical solvent for capture and separation of  $CO_2$  from gas streams.

Physical solvent – this technique is suited when  $CO_2$  is present in a high partial pressure system. The solubility of  $CO_2$  depend on pressure, temperature and solvent type because there is no reaction between the solvent and  $CO_2$ . One of the most interesting options is Morphisorb Process which uses the morpholine as solvent.

Chemical solvent – this technique is effective for removing  $CO_2$  from gas stream independent of the concentration or partial pressure of the  $CO_2$ . There is chemical reaction between  $CO_2$  and solvent by bonding and requiring energy. It is well suited to the post combustion capture when the partial pressure of  $CO_2$  is low.

Pros : independent of pressure
Cons : require energy enough for the chemical reaction to regenerate and recover CO<sub>2</sub>.

Because of the large volume of flue gas and the impartial  $CO_2$  pressure, chemical absorption appears to be a rational choice, as compared with other method. In 2003, Diao *et.al.* studied on  $CO_2$  removal by using ammonia scrubbing in an open continuous flow reactor. The removal efficiencies are higher than 90%, means that the absorption rate is fast. MEA and NH<sub>3</sub> are used as solvent. It is found that using NH<sub>3</sub> solvent has more influent on the  $CO_2$  absorption capacity than using MEA.

### 2.1.1.2 Solid Adsorbent Based Technologies

This technique is developed to improve the overall energy efficiency of  $CO_2$  capture and the separation by reducing the latent heat loads for vaporization of water that occur more than 50% in physical and chemical process. The solid sorbent is developed and the extra energy, nearly 30-40% is eliminated. Some significant solid sorbents are non-volatile amines on alumina support (The EniTechnologies), lithium orthosilicate (The Toshiba Process) sodium carbonate (The RTI Process) and zeolite – 13X (Dave and Duffy,CCSD). The mechanism for  $CO_2$  removal using lithium orthosilicate,

 $Li_4SiO_4 + CO_2 = Li_2SiO_3 + Li_2CO_3$ 

The mechanism for CO2 removal using sodium carbonate,

 $Na_2CO_3(s) + CO_2(g) + H_2O(g) = 2NaHCO_3(s)$ 

2.1.1.3 Membrane Separators

Membranes are microscopic sieves used for physical adsorbents because of its physical quality, such as porous structure and selective gas affinity. Hydrostatic pressure and concentration gradient is applied as the driving forces for gas separation. Two types of membrane technologies can be used for separating  $CO_2$  from other gases:

*Gas separation membranes* - A hydrostatic pressure is applied and then some molecules will pass through the micropores in membranes, and some molecules will be stopped due to the different permeability of gas. The disadvantage is that it may not be preferable to separate  $CO_2$  from flue gas because of the large volume of the flue gas and the compression energy requirement.

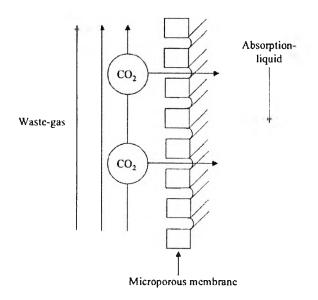


Figure 2.3 Schematic of  $CO_2$  separation using a solvent/membrane system (Dave and Duffy, CCSD).

Gas absorption membranes - A liquid sorbent is used to carry  $CO_2$  molecules pass through membrane without applying hydrostatic pressure. The counter-current of feed gas and sorbent give a greater gas-liquid contact area, so it can reduce size and cost of absorber which are important factor. Additional benefits include minimization of flooding, channeling, or foaming of liquid sorbent in the absorber.

#### 2.1.1.4 Low Temperature System

Cryogenic separation, one of these kinds uses the differences in boiling point of gases by reducing the temperature of the stream until the  $CO_2$ condenses and separates out. The critical temperature and triple point of  $CO_2$  are 31.6 °C and -56.8 °C respectively. Between these temperatures,  $CO_2$  can be liquefied by compression and cooling.

The major disadvantage of cryogenic method is high energy consumption and costs associated with gas compression and cooling.

### 2.2 Improvement Opportunities in Chemical Adsorption

### 2.2.1 <u>High Internal Phase Emulsion (PolyHIPEs)</u>

PolyHIPEs are well established class of porous and permeable materials from polymerization of monomers and cross-linking of co-monomers in the continuous phase of high internal phase emulsions (HIPEs) (Normatov *et.al.*,2007). Polymerization occurs around emulsion droplets, which create voids fraction and reach levels of 0.99 in the final material (Cameron, 2005). Size of the pores relies on degree of cross-linking, so the pore size increases whereas cross-linking is taken place but the physical stability of the porous polymer decreases. If high internal phase emulsions are dispersion of water phase (aqueous phase) in the continuous phase (oil phase), it called water-in-oil (w/o). In contrast, high internal phase emulsions are dispersion of oil phase in continuous phase; it called oil-in-water (o/w).

This kind of polymer has been prepared by many techniques. Polymerization techniques to prepare microsphere with a high specific area have three generations. The first-generation techniques, called hypercrosslinked polymer, were prepared by Friedel-Crafts reaction of chloromethyl groups on low-crosslinked polystyrene. Because the additional crosslinkers (chloromethyl methyl ether, etc.) to construct a chloromethyl group were strongly carcinogenic, this method suffered many difficulties in manufacture and application. The second-generation techniques were synthesized by divinylbenzene (DVB) copolymerization in the presence of the porogen insoluble in polymer but miscible in monomer. The maximum specific surface area of the products was often limited by purity of DVB and the mechanism of the pore formation induced by phase separation in polymerization. In 2005, Stefane and Krajnc studied on 4-vinylbenzyl chloride (VBC) 70% based water-in-oil-in-water emulsions and used DVB 30% as crosslinker. It was found that pore volume is about 85%. The third-generation techniques were purposed without using any carcinogenic crosslinkers, just by post-cosslinking of the residual function poly(divinylbenzene) groups on or (vinylbenzylchloride) microspheres (Hao et.al.,2008).

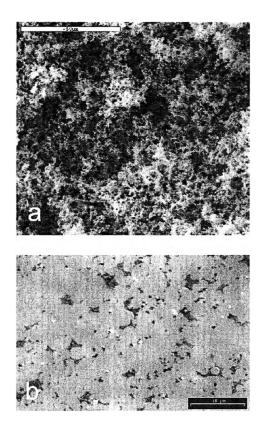
Although the advantages of polyHIPEs are high porosity but brittleness and chalkiness are still their disadvantage. In 2006, Halibach *et.al.* studied on divinylbenzene as a crosslinker and synthesized highly open porous low-density polymer foams with superior mechanical properties by the polymerization of the organic phase of concentrated emulsions. The polymers were reinforced by nanosized silica particles and the silica particles were covalently incorporated into the polymer network by adding methacryloxypropyltrimethoxysilane (MPS). The result showed that the Young's modulus of silica reinforced foams increased by 280% and the crush strength by 218% in comparison to foams without reinforcement.

In the same year, Halibach *et.al.* studied on the similar experiment but they changed the main crosslinker from divinylbenzene to polyethylene glycol dimethacrylate (PEGDMA) and got better result. The Young's modulus and the crush strength of the polymer foams increased by up to 360% and by up to 300%, respectively, in comparison to non-reinforced samples.

## 2.2.1.1 Factors Effecting Properties of PolyHIPEs

## Effect of Porogen

In 2005, Cameron studied the influence of different organic porogenic solvents on the surface area of poly (divinylbenzene). It was found that changing the solvent from toluene to chlorobenzene (CB) to 2-chloroethylbenzene (CEB) produced an increase in BET surface area from 350 to 550 m<sup>2</sup>/g. TEM images confirmed the cellular nature of the material. It appeared that the windows had become enlarged to such an extent that the cellular morphology was not obvious by SEM (Figure 2.4). An increase in window diameter is indicative of an increase in emulsion stability; this was confirmed by experiments involving compression of monolayers of the different HIPE organic phases, in which it was observed that CEB gave rise to the most densely packed interface. Although variation of the organic porogen resulted in an increase in surface area, the mechanical properties were not improved. From extensive studies, it was found that a 1:1 (v:v) mixture of CEB and CB resulted in a material with a high surface area (550 m<sup>2</sup>/g) that still retained the expected PolyHIPE morphology. Such materials were found to be substantially more robust than those prepared with CEB alone.



**Figure 2.4** (a) SEM and (b) TEM of DVB PolyHIPE prepared with CEB in the organic phase (1:1 vol. ratio to DVB) (Neil R. Cameron, 2005).

## Effect of Surfactant

In 2009, Barbetta *et.al.* synthesized polyHIPE using glycidyl methacrylate (GMA) and divinylbenzene in the presence of a porogen, and emulsion templating as the preparation technique. Two surfactants were used as the emulsion stabilizer. It turned out that the choice of the surfactant was essential for the successful synthesis of polyHIPEs containing large amount of the functional monomer GMA and characterized by a well-defined morphology. Sorbitan monooleate (SPAN 80) showed poor performances in stabilizing emulsions with a content of GMA > 40% v/v. On the contrary, polyglycerol of a fatty acid (PGE 080/D) exhibited superior performances allowing to stabilise emulsion with a GMA content up to 80% v/v. The ensuing polyHIPEs presented a well-defined morphology and surface areas very close to those of the corresponding resins of the

same composition. This proved that emulsion destabilizing phenomenon such as Ostwald ripening was effectively inhibited by PGE.

In 2005, Cameron showed that surfactant concentration has effected on the average void diameter. The increasing of surfactant concentration also results in a decrease in average void diameter due to increase emulsion stability. The using of low concentration of surfactant, closed-cell poly (styrene-DVB) PolyHIPE material could be taken place, because the increasing of surfactant concentration leads to the thinning of the monomer film separating adjacent emulsion droplet. Changing the surfactant employed from sorbitan monooleate (Span 80) to a 3-component mixture of cetyltrimethylammonium bromide (CTAB), dodecylbenzenesulfonic acid, sodium salt (DDBSS) and sorbitan monolaurate (Span 20) produced some further insights (Cameron, 2005). With this surfactant mixture, surface area values were much higher in almost every case than with Span 80 (for CB: 689 compared to 346 m<sup>2</sup>/g). Mixtures of ionic and non-ionic surfactants are known to form a more robust interfacial film around each emulsion droplet, leading to enhanced emulsion stability.

## Effect of Water Fraction

In 2008, Zhang *et.al.* found that increasing the water volume fraction ( $f_w$ ) of polyHIPEs was found to cause materials with more open porous structure. The average void diameter increased steadily, and the void diameter distributions became broad. With increase of  $f_w$ , the surfactant was required to stabilize an increasingly large interfacial area. Simultaneously, the surfactant concentration was kept constant relative to the monomer phase. Thus the average water droplet size became correspondingly larger and the average void diameters would be increased. At the same time the skeletal framework (continuous phase in HIPEs) of the solid polyHIPEs became progressively thinner, which caused a concomitant thinning of the film of continuous phase around the aqueous droplets.

2.2.1.2 Applications for PolyHIPEs (Cameron, 2005)

PolyHIPEs are important for a wide range of applications in food, cosmetic, pharmaceutical, and petroleum industries. It can be produced in many forms such as - In granular form, the use of crosslinked polystyrene PolyHIPE as a support for a polyacrylamide gel used in solid phase peptide synthesis.

- Functionalisation of the PolyHIPE surface to yield carbon-carbon double bonds led to covalent anchoring of the gel support to the rigid polystyrene matrix.

- Monolithic polystyrene PolyHIPEs employing hydrophobic reagents, is to introduce –SO3H, –Br and –NO2 groups.

- In solid form, sulfonic acid modified materials were used as solid phase acid catalysts for the hydration of cyclohexene in a two-phase liquid–liquid process.

- PolyHIPE materials are used as matrices from which to prepare electrochemical sensors.

- PolyHIPE materials have been used in biological and biomedical applications. For example, potential substrates for tissue engineering.

## 2.2.2 Biopolymer

Biopolymer is derived from naturally occurring sources, which is the exoskeleton of insects, crustaceans, and fungi. They have been shown to be biocompatible and biodegradable. These polymers are semi-synthetically derived amino polysaccharides that have unique structures, multidimensional properties, highly sophisticated functionality and a wide range of applications in biomedical and other industrial areas. They have become interesting not only an abundant renewable resource but also very compatible and effective biomaterials that are used in many applications. In this research, biopolymer is a copolymer of  $\beta$ -[1,4]-linked-2-acetamido-2-deoxy-D-glucopyranose and 2-amino-2-deoxy-D-glucopyranose which is the second most abundant natural polysaccharide. It is obtained by deacetylation of its parent polymer chitin, a polysaccharide widely distributed in nature (e.g. crustaceans, insects and certain fungi). Due to chitin's poor solubility in aqueous solution and organic solvents, it does not find practical applications. The positive facets of excellent biocompatibility and admirable biodegradability with

ecological safety and low toxicity with versatile biological activities such as antimicrobial activity and low immunogenicity have provided ample opportunities for further development (Chiellini *et.al*, 2011). The structure of this biopolymer is shown in Figure 2.5.

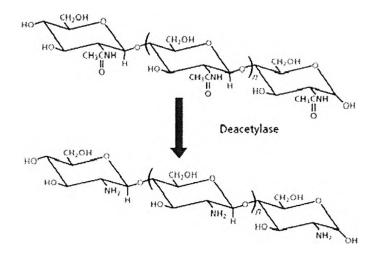


Figure 2.5 Structure of biopolymer (http://www.altakitin.com/?Products).

It is a well-known adsorbent for metal ions, such as Cu (II), Ni (II), Cr (II), Zn (II) and Hg (II), produced commercially by deacetylation of chitin using sodium hydroxide in excess as a reagent and water as a solvent. The amino group in its structure has a pKa value of ~ 6.5, which leads to a protonation in acidic to neutral solution with a charge density dependent on pH and the % DA-value. This reason makes it water soluble and a bioadhesive.

In 2003, Liu et.al. reported on the preparing macroporous chitosan membranes via the phase-inversion method by using silica gel as the porogens as shown in Figure 2.6. The ratio of silica/chitosan (g/g) has an effect on the % porosity of macroporous chitosan membranes. An increase in the silica/chitosan ratio increased the porosity of the membrane until reached a maximum when the silica/chitosan ratio was around 12. The porosity decreased when the silica/chitosan ratio exceeded 12. It was concluded that the walls of the pores became thin after the

increase of the silica/chitosan ratio, because the walls eventually fail to hold the weight of the matrix; they collapse so resulting in low porosity.

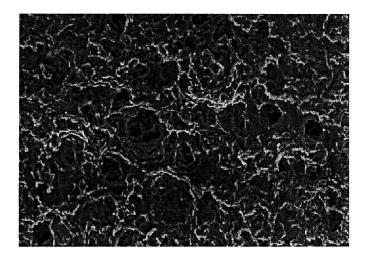


Figure 2.6 SEM photographs of macroporous chitosan membrane at surface (Liu *et.al*, 2003).

The fundamental characteristics of chitosan are very strong antibacterial effect and can be totally biodegraded. Its biocompatibility (anallergicity) and humidity absorption properties are high. The applications of biopolymer were shown in Table 2.2.

**Table 2.2**Applications of biopolymer

Wastewater Treatment	<ul><li>Removal of metal ions</li><li>Coagulant : protein, dye, and amino acids</li></ul>	
Food Industry	<ul> <li>Removal of dye, suspended solids etc.</li> <li>Preservative</li> <li>Color stabilization</li> <li>Animal feed additive</li> </ul>	
Medical	<ul> <li>Blood cholesterol control</li> <li>Controlled release of drugs</li> <li>Skin burn</li> <li>Contact lens</li> </ul>	

	- Enzyme immobilization	
Distashuslasy	- Protein separation	
Biotechnology	Cell recovery	
	- Chromatography	
	- Seed coating	
Agriculture	- Fertilizer	
	- Controller agrochemical release	
	- Moisturizer	
Cosmetics	- Face, hand, and body creams	
	- Bath lotion	
Pulp and Paper	- Surface treatment	

In 2006, Adel *et.al.* showed that addition of chitosan or its derivatives achieve an improvement in the strength properties of paper sheets before/after aging. Additions of mixture of cyanoethyl and carboxymethyl chitosan improve the mechanical properties of the produced paper sheets. Values of breaking length of treated paper sheets, with chitosan or its derivatives by the addition method during sheet formation are higher than those obtained with the dipping method.

### 2.3 Literature Review

In 2009 Lu *et.al.* studied thermodynamics and regeneration of  $CO_2$  adsorption from gas streams by using amine functionalized mesoporous sphericalsilica particles (MSP) as adsorbent. It was found that the adsorption process is endothermic in 20–60 °C, but is exothermic in 60–150 °C. The cyclic  $CO_2$ adsorption via MSP showed that the adsorbed  $CO_2$  can be effectively desorbed at 120 °C for 25 min while the adsorbed  $CO_2$  due to physical interaction can be effectively desorbed at 0.145 bar for 30 min. The desorption time of spent MSP can be further shortened to 7.5 min via a combination of thermal treatment and vacuum suction. The adsorption performance, the crystal phase and the surface functional groups of MSP were preserved during 15 cycles of adsorption and regeneration.

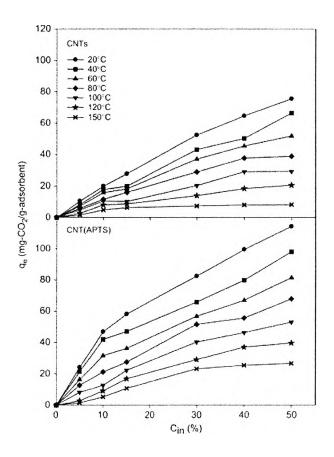
In 2009 Thiruvenkatachari *et.al.* studied post combustion  $CO_2$  capture technologies with a focus on carbon fiber monolithic composite adsorbents. It can be made in various shapes, such as a honeycomb structure having a plurality of openings or passages of any desired size or shape. This shape is known to have a very high geometric surface area to volume ratio.

Carbon fiber composite monoliths have higher affinity for carbon dioxide adsorption compared to conventional carbon based adsorbents. The adsorptive characteristics of the monoliths were also found to be dependent on the choice of precursor material (carbon fibres). Pore width was an important factor in determining  $CO_2$  adsorption, other factors such as pore volume and surface area.

In 2009, Wang *et.al.* studied on CaO-based regenerative sorbents for  $CO_2$  capture. In the water-gas shift reaction, the more carbonation/calcinations cycle can absorb more  $CO_2$ , but unfortunately the sorbent activity decay with increasing number of cycle due to sintering – loss of surface area. CaO was sorbent from the calcinations of limestone,

## $CaO + CO_2 = CaCO_3 + heat$

In 2010, Chieh Hsu *et.al.* studied in thermodynamics and regeneration of  $CO_2$  adsorption from gas streams using 3-aminopropyl-triethoxysilane functionalized carbon nanotube as adsorbent. It was found that the  $CO_2$  adsorption on CNTs and CNT (APTS) is exothermic which is typical for physical adsorption. The cyclic  $CO_2$  adsorption on CNT (APTS) showed that the adsorbed  $CO_2$  can be effectively desorbed at 120 °C for 25 min while the adsorbed  $CO_2$  due to physical interaction can be effectively desorbed at 0.145 atm. for 30 min. The adsorption isotherm of  $CO_2$  is shown in Figure 2.7. The regeneration time can be further shortened to 5 min via a thermal/vacuum desorption and thus reduces a significant amount of energy penalty. The adsorption capacity, the pore structure, the crystal phase and the surface functional groups of CNT (APTS) were preserved in the 20 cycles of adsorption and regeneration.



**Figure 2.7** Adsorption isotherms of  $CO_2$  via CNTs and CNT(APTS) at multiple temperatures. (Chieh Hsu *et.al.*,2010).

In 2010, Li *et.al.* studied  $CO_2$  adsorption on high surface area activated carbon (AC) modified by N<sub>2</sub>, H<sub>2</sub> and ammonia. It was found that the isotherms of  $CO_2$  on the AC and modified AC samples at 298K and 328K in the range of the pressures from vacuum to 30.0 bar. It can be seen that the amounts adsorbed of  $CO_2$  on all the samples decreased with increasing temperature.

In order to describe the CO<sub>2</sub> adsorption behavior on these ACs clearly, the Langmuir equation was used to fit the isotherms. The Langmuir model can be represented as follows

$$q_{i} = \frac{q_{\max}KP_{i}^{*}}{1 + KP_{i}^{*}}$$
  
or  
$$\frac{P^{*}}{q} = \frac{1}{q_{\max}K} + \frac{P^{*}}{q_{\max}K}$$

where  $q_i$  is the amount adsorbed in equilibrium with the concentration of adsorbate in gas phase (mg/g),  $q_{max}$  is the maximum adsorption amount (mg/g), P\* is the equilibrium pressure of the adsorbate in gas phase (bar), and K is the equilibrium constant of adsorption. In the model,  $q_{max}$  and K can be calculated from the linear plots of p/q versus p.

The result of fitting Langmuir equation showed that the linear correlation of the data was good because the correlation coefficients  $r^2$  were up to 0.99. It meant the adsorption behaviors of CO<sub>2</sub> on adsorbents can be well described by the Langmuir adsorption equation. The maximum adsorption capacity,  $q_{max}$  of adsorbents became lower with the increase of temperature, suggesting that the adsorption of CO<sub>2</sub> on those adsorbents was physical adsorption.

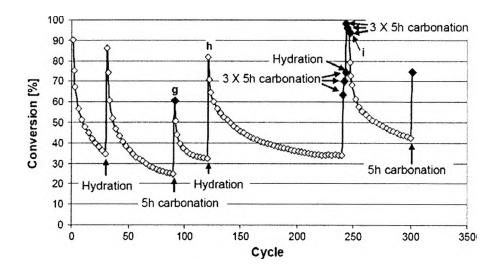
In 2010, Sayari et.al. developed an equilibrium model capable of describing  $CO_2$  adsorption isotherms on amine-grafted mesoporous silica using a semi-empirical. The result showed that  $CO_2$  adsorption occurs via two independent chemisorption and physisorption mechanisms. The semi-empirical adsorption isotherm model capable of fitting the experimental  $CO_2$  adsorption over a wide range of pressure, from as low as 0.001 to 20 bars was developed using a Toth model in its temperature-dependent form. The functionalized mesoporous materials for the  $CO_2$  adsorption were predicted based on surface area and amine loading.

In 2010, Serna-Guerrero and Sayari investigated the adsorption kinetics of  $CO_2$  on amine-functionalized mesoporous silica at low concentrations. The kinetic models were fit in a function of time at temperatures between 25 and 70 °C. There are three kinetic adsorption models in this research as shown in Table 2.3. The Avrami's kinetic model with a reaction kinetic order of 1.4 showed the best result to describe complex adsorption mechanisms and it was also demonstrated that TRI-PE-MCM-41 offers more favorable kinetics than PEI-impregnated pore expanded MCM-41 silica.

Kinetic model	Equation	Differential form
Pseudo-first order	$q_t = q_c [1 - \exp(-k_r t)]$	$\frac{dq_t}{dt} = k_f(q_t - q_t)$
Pseudo-second order	$q_t = \frac{k_z q_z^2 z}{1 + q_z k_z t}$	$\frac{dq_t}{dt} = k_t (q_c - q_t)^2$ $\frac{dq_t}{dt} = k_A^n t^{n-1} (q_c - q_t)$
Avrami	$q_t = q_r [1 - \exp(-(k_A t)^{n_A})]$	$\frac{dq_t}{dt} = k_A^n t^{n-1} (q_e - q_t)$

 Table 2.3 Kinetic adsorption models (Serna-Guerrero and Sayari, 2010)

In 2010, Wang et.al. showed the superior performance in cycles carbonation/calcinations for high-temperature  $CO_2$ capture using CaO-based pellets supported with aluminate cements as shown in Figure 2.8. It was found that after 30 cycles, pellets recovered their activity, and more interestingly after hydration stage, the pellets are more favorable to reaction. However, it also has sintering at the surface and their morphology is observed by SEM.



**Figure 2.8** The activity of sorbent in carbonation/calcinations cycles of CO<sub>2</sub> capture (Wang *et.al.*, 2010).

Since sorbent is as a way to capture  $CO_2$  from flue gas, its high  $CO_2$  carrying capacity is the most important property of synthetic sorbents but there is a problem of attrition of this material. Gonzlez *et.al.* (2010) investigated the attrition of limestone used in fluidized bed reactor. It was found that the limestone is

particularly fragile during the initial calcinations during the first few hours of circulation so the attrition properties are important for designing a system.

In this work, high surface area material loaded with purified biopolymer was synthesized by using high internal phase emulsion method. The purpose is to prepare the adsorbent from polymer-polyHIPE for carbon dioxide adsorption. Moreover, biopolymer used in this work contains primary amines which show potential for  $CO_2$  adsorption.

High porous polymer foams with a highly interconnected pore network obtained from polyHIPEs templates with purified biopolymer that had higher purity by purification. The adsorption potential was considered in term of the effect of biopolymer particle (0, 7, 11, 16, and 23 wt%) and the effect of biopolymer solution (30, 50, 70, 100, 120 and 150 wt%) in adsorbent. The amount of mixed surfactant (20, 23, and 25 %wt) was studied by adding purified biopolymer in emulsion. The adsorbents were characterized by FTIR, SEM, BET, TGA and CHN.