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ENZYMATIC REACTION KINETICS AND ADSORPTION PROCESS IN CYCLODEXTRINS PRODUCTION FROM SELECTED STARCHES

SYAHINAZ BINTI SHAHRAZI

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By

SYAHINAZ BINTI SHAHRAZI

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

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Chairman : Mohd Noriznan bin Mokhtar, PhD
Faculty : Engineering

Two main processes in Cyclodextrins (CDs) production were studied in order to improve the industrial production. These processes are the enzymatic reaction of Cyclodextrin Glycosyl Transferase (CGTase) on starch which produces a mixture of CDs and other by-products, and the adsorption process on the enzymatic product mixture to obtain single CD. The CGTase enzymatic reactions on various starches were investigated by batch mode and dynamic mathematical modelling was proposed.

Tapioca starch shows the highest CDs production of 23 g L^{-1} followed by sago (22 g L^{-1}) and corn (19 g L^{-1}) starch using 5% (w/v) initial starch concentration. From the experimental data of tapioca starch, Michaelis-Menten parameter which is also known as substrate limitation parameter, K_M (58.23, 54.07 and 7.52 g L^{-1} for α-, β- and ɣ-CD, respectively) and maximum velocity of enzymatic kinetic, V_{max} (3.45, 2.76 and 0.45 g L^{-1} min^{-1} for α-, β- and ɣ-CD, respectively) were obtained by linearization. Results show that the production of CDs was also affected by product inhibition, $K_{1,i}$ at the range of 9 to 0.8 g L^{-1} and degradation of CD rate by coupling reaction, $\delta_{CD,i}$ at the range of 0.0046 to 0.658 min^{-1}. Thus, all parameters were considered using the dynamic simulation and found that the exponential reaction kinetic model fitted the experimental data better. Results were supported by sensitivity analysis on $K_{1,i}$ parameter with impact of 8 – 18% difference from original data and validation experiment by using fed batch mode.

In adsorption process, experimental results show the highest adsorption of α-CDs (700 mg g^{-1}) was at low temperature (20˚C) and as temperature increase up to 50˚C, the adsorption of α-CDs reduce until 400 mg g^{-1}. Fractogel EMD-Phenyl retained α-CD as temperature increase from 20 until 50˚C, thus can be separated from β- and ɣ-CD. Adsorption of CDs onto Fractogel EMD-Phenyl adsorbent was preferred when compared to activated carbon (AC). The kinetic and isotherm adsorption studies were done by fitting the adsorption data with several models. The kinetic adsorption of CDs onto Fractogel EMD-Phenyl

could be described by the pseudo-second-order kinetics model with R^2 value of > 0.94 and SSE value < 28. The adsorption equilibrium data obeys the Temkin isotherm model with R^2 value of > 0.84 and SSE value was less than 30.23. The adsorption activation energies obtained were at the range of 3 - 40 kJ mol^{-1}.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

KINETIK TINDAKBALAS ENZIM DAN PROSES PENJERAPAN DI DALAM PENGHASILAN "CYCLODEXTRIN" DARI KANJI BERLAINAN

Oleh

SYAHINAZ BINTI SHAHRAZI

April 2015

Pengerusi : Mohd Noriznan bin Mokhtar, PhD
Fakulti : Kejuruteraan

Dua proses penghasilan "Cyclodextrin" CDs yang amat penting diselidik untuk memperbaiki penghasilan di peringkat industri. Proses tersebut adalah tindakbalas enzim "Cyclodextrin Glycosyl Transferase (CGTase)" keatas kanji yang menghasilkan campuran CDs dan produk sampingan lain, dan proses penjerapan keatas produk yang diperolehi dari tindakbalas enzim untuk memperolehi CD tunggal. Tindakbalas enzim CGTase keatas pelbagai kanji disiasat menggunakan "batch mode" dan model matematik dinamik yang sesuai dicadangkan.

Kanji ubi kayu menghasikan CDs yang paling tinggi iaitu 23 g L^{-1} diikuti dengan sagu (22 g L^{-1}) dan jagung (19 g L^{-1}) apabila menggunakan 5% (w/v) kepekatan awal kanji. Berdasarkan data eksperimen kanji ubi kayu, parameter Michaelis-menten atau juga dikenali sebagai parameter had substrat, K_M (58.23, 54.07 and 7.52 g L^{-1} for α-, β- and ɣ-CD masing-masing) dan had laju maksimum kinetik enzim, V_{max} (3.45, 2.76 and 0.45 g L^{-1} min^{-1} for α-, β- and ɣ-CD masing-masing) diperolehi menggunakan kaedah "linearization". Keputusan eksperimen menunjukkan parameter perencatan oleh produk, $K_{1,i}$ dari julat 9 hingga 0.8 g L^{-1} dan degradasi CD yang disebabkan oleh tindakbalas "coupling", $\delta_{CD,i}$ dari julat 0.0046 hingga 0.658 min^{-1} memberi kesan terhadap penghasilan CDs. Oleh yang demikian, kedua-dua parameter perlu diambil kira didalam model dan kinetik tindakbalas eksponen dan data eksperimen memberi kepadanan yang paling baik menggunakan simulasi dinamik. Keputusan ini disokong oleh analisa kepekaan pada parameter $K_{1,i}$ dengan impak paling tinggi 8 – 18% perbezaan dari data asal dan eksperimen validasi telah dijalankan menggunakan mod "fed batch".

Bagi proses penjerapan pula, hasil eksperimen menunjukkan kadar penjerapan α-CDs tertinggi (700 mg g^{-1}) adalah pada suhu rendah (20˚C) dan apabila suhu bertambah sehingga 50˚C, kadar penjerapan α-CDs berkurang kepada 400 mg g^{-1}. α-CD melekat pada "Fractogel EMD-Phenyl" lebih lama walaupun suhu meningkat dari 20 sehingga 50 ˚C, maka ia boleh diasingkan dari β- dan ɣ-CD.

Penjerapan CDs pada bahan penjerap “Fractogel EMD-Phenyl” dipilih jika dibandingkan dengan “Activated carbon” (AC). Kajian terhadap kinetic dan isotherma penjerapan dilakukan dan data dibandingkan dengan beberapa model. Kinetik penjerapan CDs pada Fractogel EMD-Phenyl boleh diterangkan menggunakan model tindakbalas tertib kedua “pseudo” dengan nilai $R^2 > 0.94$ dan SSE < 28. Data keseimbangan jerapan mematuhi model isoterma Temkin dengan nilai $R^2 > 0.84$ dan SSE < 30.23. Tenaga pengaktifan bagi proses penjerapan yang diperolehi adalah dalam linkungan 3 - 40 kJ mol^{-1}.

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I certify that a Thesis Examination Committee has met on 30 April 2015 to conduct the final examination of Syahinaz binti Shahrazi on her thesis entitled "Enzymatic Reaction Kinetics and Adsorption Process in Cyclodextrins Production from Selected Starches" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

Members of the Thesis Examination Committee were as follows:

Mohd Nordin bin Ibrahim, PhD
Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

Chin Nyuk Ling, PhD
Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Internal Examiner)

Siti Mazlina binti Mustapa Kamal, PhD
Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Internal Examiner)

Maizirwan Mel, PhD
Associate Professor
Universiti Islam Antarabangsa Malaysia
Malaysia
(External Examiner)

ZULKARNAIN ZAINAL, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 12 August 2015

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

Mohd Noriznan bin Mokhtar, PhD
Senior Lecturer
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

Farah Saleena binti Taip, PhD
Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Member)

Khairul Faezah binti Md. Yunos, PhD
Senior Lecturer
Faculty of Engineering
Universiti Putra Malaysia
(Member)

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Signature:

Name of Member of Supervisory Committee: Khairul Faezah binti Md. Yunos, PhD

Signature:

Name of Member of Supervisory Committee: Associate Professor Farah Saleena binti Taip, PhD

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$\delta_{CD,i}$	Degradation coefficient rate of component *i* (1/min)
b	Constant heat of adsorption (J/mol)
B_T	Temkin constant
c_E	Enzyme activity in the bioreactor (U /L)
c_i	concentration of the component *i* in the bioreactor (g/L)
$c_{in,Ej}$	Enzyme activity from inlet *j* (U /L)
$c_{in,ij}$	Concentration of component *i* from inlet *j* (g/L)
C_0	Initial concentration of CDs (mg mL^{-1})
C_e	Equilibrium concentration of CDs in the solution (mg mL^{-1})
C_t	Concentration of mixture at time t (mg mL^{-1})
d	Diameter of the bioreactor (cm)
E_a	Activation energy (J mol^{-1} K^{-1})
h_f	Height of the reaction solution in the bioreactor (cm)
K_0	Pre-exponential factor
$K_{1,i}$	Product inhibition constant of component *i* (g/L)
$K_{cat,i}$	Kinetic constant of component *i* (g/U.min)
K_F	Freundlich constant (mg g^{-1})
K_{id}	Intraparticle diffusion rate constant (mg g^{-1} $min^{-1/2}$)
K_L	Langmuir constant (L mg^{-1})
$K_{M,i}$	Michaelis-Menten constant of component *i* (g/L)
K_{P1}	Pseudo-first-order rate constant (min^{-1})
K_{P2}	Pseudo-second-order adsorption rate constant (g mg^{-1} min^{-1}).
K_T	Temkin isotherm constant (L g^{-1})
m	Mass of adsorbent (g)
m_E	Enzyme activity (U)

m_i	Mass of component *i* (g)
n	Associated adsorption intensity
N	Number of data point
Q_e	Total amount of CDs adsorbed by 1 g of adsorbent at equilibrium (mg g^{-1})
Q_m	Maximum single layer adsorption capacity (mg g^{-1})
Q_t	CD adsorbed per gram adsorbent at time t (mg g^{-1})
$r_{CD,i}$	Production rate of cyclodextrin *i* (g/L.min)
r_E	Decay rate of enzyme (U /min)
r_i	Reaction rate of component *i* (g/L.min)
R	Universal gas constant (8.3144 J mol^{-1} K^{-1})
R_L	Separation factor
t	Time (min)
T	Temperature (Kelvin)
V	Volume of the solution (mL)
$V_{0,i}$	Initial velocity of enzyme kinetic (g/L.min)
V_f	Working volume in the bioreactor (L)
ν_i	Stoichiometry coefficient of component *i*
$V_{max,i}$	Maximum velocity of enzyme kinetic on component *i* (g/L.min)
$\dot{V}_{in,j}$	Volumetric flow rate of inlet *j* into the bioreactor (L/min)
$\dot{V}_{out}$	Volumetric flow rate of bioreactor outlet (L/min)

CHAPTER 1

INTRODUCTION

1.1. Introduction of Cyclodextrins

Cyclodextrins (CDs) which also known as Schardinger dextrins or cycloamyloses (Seres *et al.*, 1989) are made up of sugar molecules bound together by α –(1,4) glycosidic bond in a ring called the cyclic oligosaccharides (Figure 1.1). There are 3 main types of CDs: alpha- (α-), beta- (β-), and gamma–CD (ɣ-CD) which composed of 6, 7, and 8 α-(1,4)-linked glycosyl units, respectively. The shape of CDs can be described as truncated cones ("bucket shaped") as shown in Figure 1.1. The hydroxyl functions are oriented to the cone exterior with wider end bears the secondary C_2 and C_3 hydroxyl groups and the primary C_6 hydroxyl groups are located at the narrow end of the CD ring (Martin Del Valle, 2003).

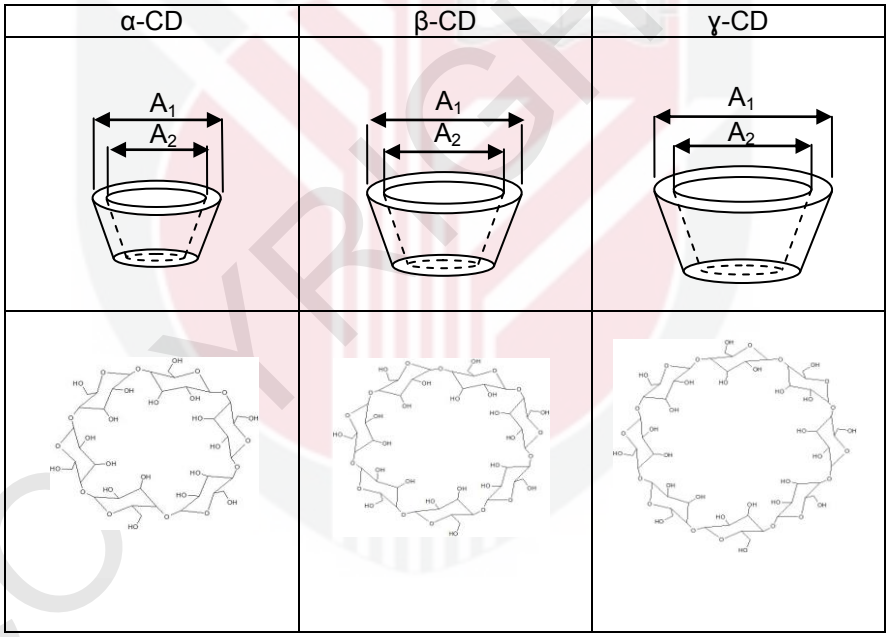

Figure 1.1: Structure of CDs (Sources: Martin Del Valle, 2003)

The hydrophilic outside surface of CDs can make them dissolved in water (Brewster and Loftsson, 2007) while the central cavity of CD is lined with skeletal carbons and oxygen of the glucose which give hydrophobic (lipophilic) character (Martin Del Valle, 2003; Atasanova *et al*., 2009). The detailed properties of each CDs were given in Table 1.1. All three CDs have similar height of 0.78nm (Tsuchiyama *et al.*, 1991b).

The main interest in CDs is at their ability to form inclusion complexes with several compounds (Brewster and Loftsson, 2007). Inclusion complexes are

compounds which form a host-guest relationship between an aqueous solution of the CD and the guest compound. It is known that different guest compound have different affinities towards the host CD (Beesley, 1989).

Table 1.1: Properties of CDs (Martin Del Valle, 2003)

	α-CD	β-CD	ɣ-CD
Glucopyranose units	6	7	8
Empirical formula (anhydrous)	$C_{36}H_{60}O_{30}$	$C_{42}H7_0O_{35}$	$C_{48}H_{80}O_{40}$
Molecular weight (g/mol)	972.85	1134.99	1297.14
Solubility in water (g/L) at 25˚C	145	18.5	232
Outer diameter (A_1)	14.6	15.4	17.5
Cavity diameter (A_2)	4.7-5.3	6.0-6.5	7.5-8.3
Cavity volume (A^3)	174	262	427

CDs are able to form inclusion complexes with a wide variety of hydrophobic guest molecules through its hydrophobic cavity (Brewster and Loftsson, 2007; Van der Veen et at., 2000) primarily with organic molecules with a function of 2 key factors. The first factor is the relative size of the cavity of CD to the size of the guest molecule or the functional group of the adsorbent. The second critical factor is the thermodynamic interactions of the different components on the system (Brewster and Loftsson, 2007).

Due to their ability to form inclusion complexes with variety of chemical, they are in great interest for food, pharmaceutical, chemical, cosmetic and agricultural industries (Brewster and Loftsson, 2007). Since the three CDs have different cavity size, each CD has its own range of guest which they will form an improved aqueous solubility complexes (Nicolescu *et al.*, 2010). According to U.S Food and Drug Administration (FDA), α-CD can be used for fiber supplement in selected solid, semi-liquid, and liquid foods. Moreover, α-CD also has nutritional properties similar to fermentable dietary fiber. α-CD mainly be used as a carrier or stabilizer for flavors (flavor adjuvant), colors, vitamins and fatty acids, and can improve mouth-feel in beverages (FDA,2013a). β-CD can be used as flavor carriers and protectant (FDA, 2013b). For ɣ-CD, it can be applied as a stabilizer, emulsifier, carrier and formulation aid in consumable product (FDA, 2013c).

CDs can be produced by means of enzymatic conversion of starch by using Cyclodextrin Glycosyl Transferase (CGTase) enzyme at the appropriate pH, temperature and time. CGTase is generally an extracellular enzyme found in bacteria (Tonkova, 1998). The CGTase enzymes degrade the gelatinized starch by catalyzing the cyclization, an intramolecular transglycosylation reaction. Besides, it also undergoes coupling, disproportionation reactions, and a weak hydrolytic activity. Thus, the CGTase enzymatic reaction produces a mixture of α-, β-, ɣ-CD and other by-products, linear dextrins and unreacted starch (Szejtli, 1982). In order to obtain single size of CD, several separation steps are required. CD can be separated by using either solvent method that

used chemical solution to form selected CD's precipitate or non-solvent method. The overall process of CDs production is shown in Figure 1.2.

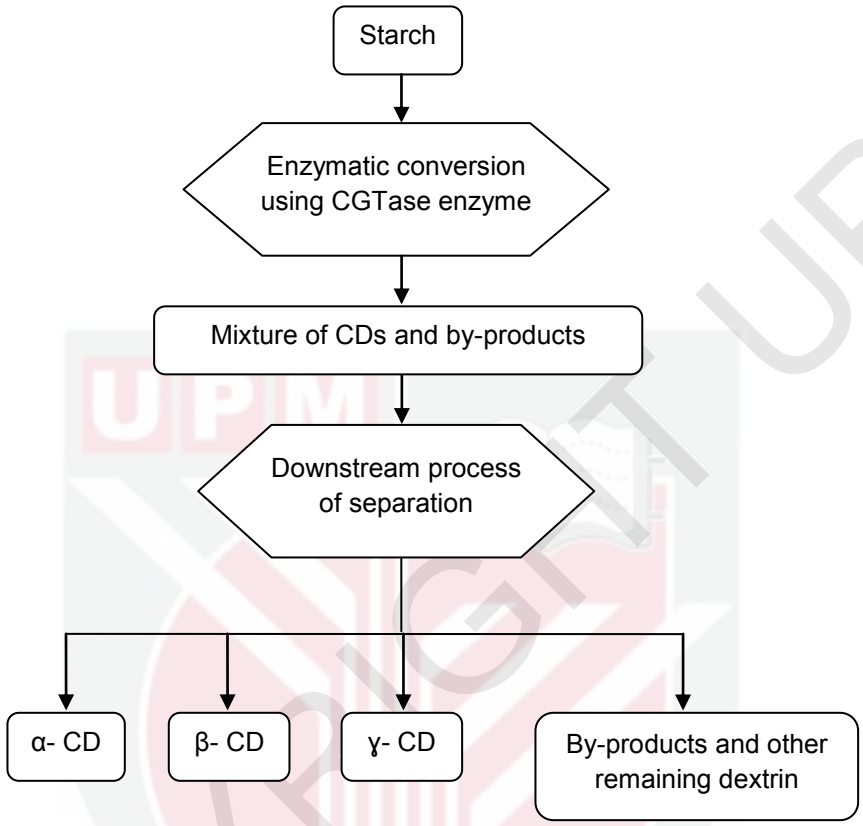

Figure 1.2: Production step of CDs.

1.2. Market Research

Most CD sold and used currently is β-CD since its price is the cheapest compared to α- and ɣ-CD. The price of β-CD has reduced significantly due to its easy purification step. β-CD cost around RM 14.20/g, α-CD RM 171/g and ɣ-CD RM 1614/g (Sigma Aldrich, 2015). Due to the lowest price, β-CD is the most accessible, while market shares of α- and ɣ-CD increase significantly (Beesley, 1989; Brewster and Loftsson, 2007). However, α- and ɣ-CD are safer to be applied in food and consumable industry as claimed by FDA (FDA, 2013a). Hence, more research on α- and ɣ-CDs is needed since their demand is increasing (Biwer et at., 2002).

1.3. Problem Statement

Many studies on newly develop CGTase from different sources had been done to accomplish the economical process of CDs (Sian *et al.* 2005; Savagare *et al.*, 2008; Zhekova *et al.*, 2008; Zhekova and Stanchev, 2011). α-CD production has been studied using different types of CGTase such as *Bacillus macerans* (Tsuchiyama *et al.*, 1991; Terada *et al.*, 1997; Yamamoto *et al.*, 2000), *Klebsiella oxytoca* strain (Bär *et al.*, 2004) and *Paenibacillus macerans* (Cheng *et al.*, 2011; Ivanova, 2010).

By studying the detail kinetic of the enzymatic reaction using the available CGTase, CD production can be improved and optimized. The detail kinetic studies include the cyclization, coupling, disproportion and hydrolytic reaction of CGTase which occur simultaneously during the enzymatic process. CDs are formed just as the intermediate products and linear dextrin as the final products. Thus, it is crucial to control the process of conversion of starch into CDs starting from the substrate preparation until its conversion. However, very limited information details on reaction kinetic model of CGTase can be found.

A mathematical model of the CGTase production was proposed by Burhan *et al.* (2005). But, this developed model focuses only on the microbial CGTase production. Meanwhile, Cheirsilp *et al.* (2010) had studied on the kinetic parameters of the maximum velocity of enzyme kinetic (V_{max}) and Michaelis-Menten constant (K_M) for β-CD production from several starch sources using Michaelis-Menten equation. Muria *et al.* (2011) had further Cheirsilp's studies by applying the same enzyme and developed a mathematical model for CD production. However, the model only emphasises on β-CD production as mentioned by Cheirsilp *et al.* (2010). During the production of CDs, α-, β- and ɣ-CD are produced simultaneously. So, detailed models that consider all three main types of CDs need to be proposed. Furthermore, in Muria's work, the mathematical model developed considers only the substrate concentration and temperature effect but does not consider the product inhibitor parameters. Product inhibition have significant effect on the production of CDs, thus need to take into account in the CDs production model.

In the downstream process, a non-solvent separation method is preferred since it eliminates the usage of chemical. Many researches was done using non-solvent method such as ultrafiltration treatment (Hokse, 1984; Kobayashi, 1985; Yamamoto, 1988), ion-exchange chromatography (Horikoshi *et al.*, 1980; Yamamoto & Horikoshi, 1981; Okada, 1983) and affinity chromatography (Beesley, 1989; Tsuchiyama *et al.* 1991a; 1991b).

Only few studies had been done on the adsorption of CDs by using adsorption method especially the hydrophobic adsorbent. Some of the hydrophobic adsorbents used are chitosan beads with stearic acid ligand (Tsuchiyama *et al.*, 1991b), Amberlite XAD-2 and -4 (Yamamoto and Horikoshi, 1981). Their findings show that adsorption method is able to separate α-CD from the CGTase enzymatic product mixture. Tsuchiyama *et al.* (1991b) also proposed a system which reduces the process step. However, no detailed studied were

done on the kinetics and isotherm of the CD adsorption which were important in describing the adsorption process.

1.4. Objective

The general objectives of this research are to investigate the enzymatic synthesis of CDs from stach by using CGTase enzyme and to investigate the CDs adsorption on selected adsorbent for separation process.

The specific objectives are:

1. To study the mathematical kinetic modeling for α-CDs production from sago, tapioca and corn sources by CGTase enzyme;

2. To study the kinetics and isotherm of α-CDs adsorption on Fractogel EMD-Phenyl and Activated Carbon (AC) by varying temperature.

1.5. Scope of Work

In this thesis, work conducted for mathematical modeling considers all α-, β- and ɣ-CD production, but detail study focuses on α-CD production. Substrate use for CGTase enzymatic synthesis is limited to sago, corn and tapioca starch due to high amylopectin which can give high yield of CDs and they are easily available in Malaysia. For CDs adsorption process, two adsorbent were selected to be further study and compared. Both adsorbent have hydrophobic characteristic that will attract hydrophobic cavity of CDs. Experiment on kinetics and isotherm characteristic of the CDs adsorption were important to study the CDs adsorption onto the adsorbent.

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