การเตรียมตัวดูดซับจากกากตะกอนเพื่อการขจัดแก๊สแอมโมเนีย

นางสาวกัญญ์ชลา กีรติรวี

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาเคมี ภาควิชาเคมี
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2554
ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

PREPARATION OF SEWAGE SLUDGE-BASED ADSORBENT
FOR AMMONIA GAS REMOVAL

Miss Kanchalar Keeratirawee

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Chemistry
Department of Chemistry
Faculty of Science
Chulalongkorn University
Academic Year 2011

Thesis Title   PREPARATION OF SEWAGE SLUDGE-BASED
                                    ADSORBENT FOR AMMONIA GAS REMOVAL

By   Miss Kanchalar Keeratirawee

Field of Study   Chemistry

Thesis Advisor   Assistant Professor Fuangfa Unob, Ph.D.

          Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

……..………………………………… Dean of the Faculty of Science
(Professor Supot Hannongbua, Dr.rer.nat)

THESIS COMMITTEE

…………………………………………….. Chairman
(Assistant Professor Warinthorn Chavasiri, Ph.D.)

…………………………………………….. Thesis Advisor
(Assistant Professor Fuangfa Unob, Ph.D.)

…………………………………………….. Examiner
(Assistant Professor Narong Praphairaksit, Ph.D.)

…………………………….……………….External Examiner
(Patcharawadee Suwanathada, Ph.D.)

กัญญ์ชลา กีรติรวี : การเตรียมตัวดูดซับจากกากตะกอนเพื่อการขจัดแก๊สแอมโมเนีย. (PREPARATION OF SEWAGE SLUDGE-BASED ADSORBENT FOR AMMONIA GAS REMOVAL) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ.ดร.เฟื่องฟ้า อุ่นอบ, 70 หน้า.

ทำการเตรียมตัวดูดซับจากกากตะกอนที่เหลือทิ้งจากโรงบำบัดน้ำเสีย เพื่อใช้ในการดูดซับแก๊สแอมโมเนีย ด้วยการเผากากตะกอนภายใต้ภาวะที่มีอากาศและดัดแปรผิวด้วยกรดฟอสฟอริก กรดซัลฟิวริก หรือซิงก์คลอไรด์ ตรวจหาลักษณะทางกายภาพของตัวดูดซับที่เตรียมได้ด้วยวิธีการวิเคราะห์สมบัติทางความร้อน กล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด การวิเคราะห์หาพื้นที่ผิว และตรวจหาลักษณะทางเคมีของตัวดูดซับที่เตรียมได้ด้วยการไทเทรตและอะตอมมิกแอบซอร์พชันสเปกโทรสโกปี โดยศึกษาประสิทธิภาพของตัวดูดซับในการดูดซับแก๊สแอมโมเนียด้วยระบบคอลัมน์ พบว่ากากตะกอนที่ได้หลังจากการเผามีพื้นที่ผิวและปริมาณคาร์บอนเพิ่มมากขึ้น สภาวะที่เหมาะสมในการเตรียมตัวดูดซับเพื่อการขจัดแก๊สแอมโมเนียคือการเผากากตะกอนที่อุณหภูมิ 500 องศาเซลเซียส โดยใช้ความเข้มข้นของกรดหรือซิงก์คลอไรด์ที่ 3 โมลาร์ ความจุในการดูดซับของแก๊สแอมโมเนียของกากตะกอนที่เตรียมได้ด้วยการดัดแปรผิวด้วยกรดฟอสฟอริก กรดซัลฟิวริก และซิงก์คลอไรด์ คือ 81.95, 90.59, 109.78 มิลลิกรัมต่อกรัม ตามลำดับ นอกจากนั้นความเข้มข้นเริ่มต้นของแอมโมเนียและขนาดของคอลัมน์ที่ใช้ยังส่งผลต่อประสิทธิภาพการดูดซับแก๊สแอมโมเนีย โดยกลไกในการเกิดการดูดซับแอมโมเนียบนพื้นผิวที่ดัดแปรด้วยกรดและซิงก์คลอไรด์จะเกิดผ่านปฏิกิริยากรด เบส และการเกิดสารประกอบเชิงซ้อน $ZnCl_2 \bullet NH_4Cl$ บนพื้นผิว ตามลำดับ

ภาควิชา ....เคมี............ ลายมือชื่อนิสิต ....

สาขาวิชา ....เคมี............ ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก ....

ปีการศึกษา ......2554......

5272217323 : MAJOR CHEMISTRY

KEYWORDS : AMMONIA GAS/ SEWAGE SLUDGE / ADSORPTION

KANCHALAR KEERATIRAWEE: PREPARATION OF SEWAGE SLUDGE-BASED ADSORBENT FOR AMMONIA GAS REMOVAL. ADVISOR: ASST.PROF. FUANGFA UNOB, Ph.D., 70 pp.

Adsorbents derived from waste sewage sludge for ammonia gas removal were prepared by carbonization under air atmosphere and modification with H_3PO_4, H_2SO_4 or $ZnCl_2$. The physical properties of obtained adsorbents were characterized by thermogravimetric analysis, scanning electron microscopy and surface area analysis and the chemical properties by titration method and flame atomic absorption spectroscopy. The ammonia adsorption study was carried out in a fixed bed reactor. The surface area and the fixed carbon content of adsorbents increased after carbonization. The suitable condition for adsorbent preparation was the carbonization at 500 °C and modification with 3M of H_3PO_4, H_2SO_4 and $ZnCl_2$, the ammonia adsorption efficiency of the adsorbents was found to be 81.95, 90.59, 109.78 mg/g, respectively. The initial ammonia concentration and column size strongly affected the adsorption efficiency. The mechanism of ammonia adsorption on acid and $ZnCl_2$ modified adsorbents occurred via Brønsted-Lowry acid-base reaction and the formation of $ZnCl_2 \cdot NH_4Cl$ on surface.

Department: ....Chemistry....................   Student's Signature ....

Field of Study : ....Chemistry....................   Advisor's Signature ....

Academic Year : .....2011....................

ACKNOWLEDGEMENTS

My research can be successfully completed with helpfulness and support from my respectful thesis advisor, Assistant Professor Dr. Fuangfa Unob, for constructive criticism, inspiration, and encouragement during my research and have been giving useful advisements for solving many problems through my experiments. With her informal relationship, insightful discussions and suggestions make me pleasure and be joyous to my progress laboratory skill. I would like to extend my appreciation to Assistant Professor Dr. Wanlapa Aeungmitrepirom and Assistant Professor Dr. Apichat Imyim for their precious suggestions. I would like to express my sincere appreciation for them with my great thankfulness. Additionally, I gratefully acknowledge my thesis committees, videlicet, Assistant Professor Dr. Warinthorn Chavasiri, Assistant Professor Dr. Narong Praphairaksit, and Dr. Patcharawadee Suwanthada, who give me opinions and valuable suggestions for my work and devote their valuable time for my thesis defense examination. Furthermore, sincere thanks to all members of EARU (Environmental Analysis Research Unit) for their kindness, encouragement and lovely friendship, and the good supports and suggestion concerning experimental techniques particularly from Dr. Mahitti Puanngam, Miss Dussadee Ruamsanit, Miss Warangkana Kaodee, Miss Jarinya Sithiwong and Mr. Kittipong Sanuwong. I would like to thank my all classmates in Master degree of Analytical chemistry, who gave me spirituality and helpfulness for doing my work until my research was completely finished. This thesis was financially supported by CU Graduated School Thesis Grant and Center for petroleum, Petrochemicals and Advanced Materials.

And not forgotten to utter mention, I would like to thank my beloved family, especially my lovely parents who have been giving me many supports and great willingness for further my lab until success comes. The usefulness of this work, I dedicate to my parents and all the teachers who have taught me since my childhood.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SCHEMES

LIST OF ABBREVIATIONS

°C	Degree Celsius
ºF	Degree Fahrenheit
g	Gram
mg	Milligram
min	Minute
mL	Milliliter
ppm	Part per million
TGA	Thermogravimetric analysis
FAAS	Flame atomic absorption spectroscopy
SEM	Scanning electron microscopy
FT-IR	Fourier transforms infrared spectroscopy
BET	Brunauer emmett teller
IUPAC	International Union of Pure and Applied Chemistry

CHAPTER I

INTRODUCTION

1.1   Statement of purpose

Ammonia is widely used in commerce and many industries. It is commonly used in refrigeration systems, petrochemical production, rubber production, and the food and beverage industry [1-4]. Furthermore, ammonia is also released naturally from living things, particularly from agricultural activities. These activities include animal excrement, livestock housing and fertilizer application [1-3]. Since ammonia is toxic for humans and the environment, treating ammonia is strongly recommended.

Ammonia is a colorless gas with a sharp odor. Due to its corrosive properties, either leak or uncontrolled level of ammonia can be harmful to human health and can cause irritation or burns. Inhalation of ammonia vapor in sufficient quantities can be a cause of death. Considering the effects of ammonia, the regulation of ammonia vapor restriction became more stringent recently. The ACGIH (American Conference of Governmental Industrial Hygienists) has limited ammonia exposure that can be harmful to human being by a time-weighted average (TWA) of 25 ppm and a short-term exposure limit (STEL) of 35 ppm [5]. Several techniques have been used to remove the ammonia in gaseous emissions. One such technique is biofiltration, which uses billions of microorganisms on filter media to trap the ammonia vapor and convert it to a nonhazardous compound [6]. Another technique is scrubbing, which is the neutralization of ammonia by acid solution [7]. Among these techniques, adsorption technology has been widely used for the treatment of ammonia gas because it is a simple and efficient method.

Ammonia vapor can be adsorbed on different type of adsorbents such as zeolite, alumina and carbonaceous materials [8]. Ammonia vapor can also be efficiently removed by activated carbon, which has been a subject of interest in many industries. Activated carbon holds strong advantages in high surface area material. It

can be produced from carbonaceous materials, such as palm shells, coconut shells, bark [4], sewage sludge, etc. [9]. The operation costs of the production process, however, are quite expensive. From an economic point of view, the production of low cost adsorbent from waste material is a valuable option that must be taken into account. It would also satisfy modern environmental concerns.

In recent year, a growing attention to produce the adsorbent from waste materials or agricultural by-products has attracted much interest as reported in many publications [9]. Sewage sludge generated from wastewater treatment plants is one source of carbonaceous waste materials. It has been chosen as a starting material for producing adsorbents in many research experiments. The use of sewage sludge for producing adsorbent was first recognized in 1971 by Kemmer *et.al.*, they patented a process for producing adsorbents by the chemical activation for total organic carbon (TOC) removal from water [10]. In the same year, Beeckmans and Park first studied the production of adsorbent materials from sewage sludge using the carbonization method for COD and crystal violet dye adsorption [9]. Furthermore, the adsorbents derived from sewage sludge have been prepared and used for SO_2, H_2S and NO_2 gas removal. The results indicated that sewage sludge-based adsorbent provided performance that can be comparable to a commercial activated carbon [11]. As far as our knowledge, the preparation of adsorbent from sewage sludge for ammonia gas removal has not been reported.

It has been reported that the adsorption of ammonia depends on the physical and chemical properties of particular adsorbent materials. The physical property largely relies on porosity of adsorbent materials whereas the chemical property relies on the chemical functional groups on materials that lead to reactions between ammonia and adsorbent surface [12]. Since ammonia is a Brønsted-Lowry base, a simple way to improve ammonia uptake is the introduction of acidic groups on surface. H_2SO_4 and H_3PO_4 were the most widely used activating agents in the preparation of adsorbents for impurity separation application [9]. Owing to their acidic property, it can provide an acidic functional group on surface, which easily reacts with ammonia spontaneously. Additionally, $ZnCl_2$ which is one of the most effective chemical activating reagents used to increase sorbent porosity [9], could also be used as a modifying agent for ammonia gas removal. The results revealed that

activated carbon modified with $ZnCl_2$ has a better performance over unmodified activated carbon [13]. Therefore, this research aims to prepare adsorbent from sewage sludge modified with H_2SO_4, H_3PO_4 and $ZnCl_2$ for ammonia gas removal. The adsorption of ammonia on adsorbents would occur via interaction between ammonia and $ZnCl_2$ or between ammonia and acid components on the surface.

1.2   Objectives

1. To prepare adsorbents for ammonia gas removal by surface modification of spent sewage sludge from municipal wastewater treatment station.

2. To study the effect of adsorption parameters on ammonia removal by the modified adsorbents.

1.3   Scopes of this research

The scope of this research covers preparation and characterization of adsorbent derived from sewage sludge from a wastewater treatment plant and ammonia gas adsorption study. The sewage sludge was carbonized at 300 or 500 °C and further chemically modified with H_2SO_4, H_3PO_4 or $ZnCl_2$ at room temperature. The physical properties of obtained adsorbents are characterized by surface area analysis (BET method), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA) whereas the chemical properties are characterized by titration method, flame atomic absorption spectroscopy (FAAS) and Fourier transforms infrared spectroscopy (FT-IR). The adsorbents are ultimately used as adsorbent for ammonia gas removal. Ammonia gas adsorption is carried out in a fixed bed reactor. Adsorption capacity of the adsorbents, breakthrough curve and effect of the inlet concentration of ammonia are observed.

1.4   The benefit of this research

To obtain low cost sewage sludge-based adsorbents for ammonia gas removal.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Ammonia

2.1.1 Properties of ammonia

Ammonia molecule is an inorganic compound composed of one nitrogen atom covalently bound to three hydrogen atoms with a chemical formula of NH_3. As a polar molecule, it can be dissolved in polar solvent like water. Gaseous ammonia is a basic compound, it reacts spontaneously with acidic compounds such as hydrochloric acid (HCl), nitric acid (HNO_3), nitrous acid (HNO_2) or sulfuric acid (H_2SO_4) to form ammonium salts of particle size smaller than 2.5 μm in the atmospheric system [12]. Its physical properties are listed in Table 2.1.

Table 2.1 Physical properties of ammonia [13]

Physical properties	
Molar mass	17.0 g/mol
Melting point	−77.73 °C, -107.8 °F
Boiling point	−33.34 °C, -28 °F
Vapor pressure	8500 mm Hg, 20 °C, 68 °F
Specific gravity	0.77, 0 °C, 32 °F

2.1.2 Sources of ammonia

2.1.2.1 Anthropogenic sources

The major anthropogenic sources of ammonia are agriculture industry, manufacturing industry, sewage treatment plants and refrigeration systems [14]. The most abundant sources of ammonia emission are agriculture sources such as the application of chemical livestock, fertilizer application, chemical and product manufacturing recycling activities and the other sources of ammonia emission. In Asia, China and India are the major emission sources of ammonia, the total emission is 24,608 kilotons. In China, ammonia emission is higher than in India, and it is about 55% of the total ammonia emission in Asia. The largest sources of ammonia emission in China are fertilizer (46%), livestock (29%) and fuel combustion (19.5%). Livestock is the major source of ammonia emission in the United States, accounting for about 55% followed by 25% from unknown source and additional 7% from fertilizer application. Figure 2.2 and 2.3 show the ammonia emission inventory for the United States and China, respectively [15, 16]. Moreover, in European countries especially in the UK, the emission of ammonia has been estimated according to the industrial activities as listed in Table 2.2.
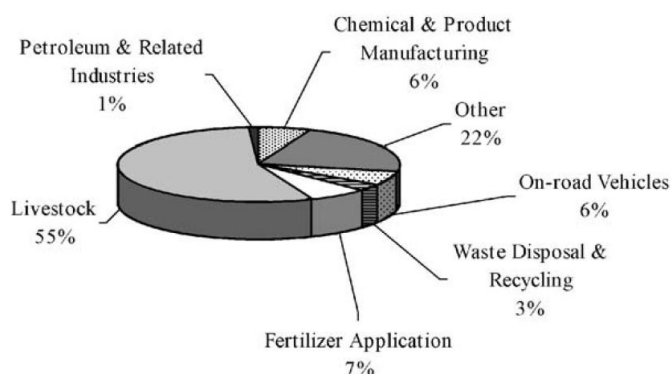
Figure 2.1 Ammonia emission inventory for the United States [15].
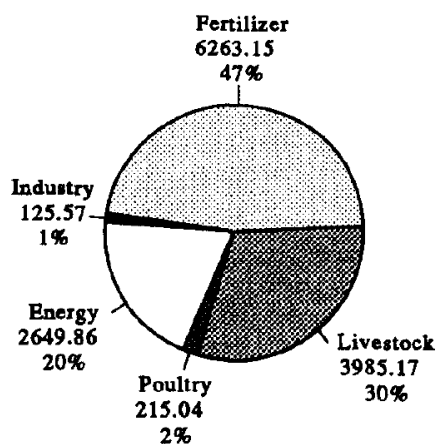
Figure 2.2 Ammonia emission inventory for China [16].

Table 2.2 Ammonia emission inventory from industrial sources in the UK [17]

Source	Best estimate (t NH$_3$-N/yr)
Mineral industries	261
Fuel and power production	163
Metal production and processing	351
Chemical industry	
Manufacture and use of organic chemicals	1651
Inorganic chemical processes	2436
Chemical fertilizer production	2952
Petrochemical, acid and halogen processes	128
Waste disposal and recycling	0.05
Paper/pulp manufacture, coating and printing	3.4
All recorded industry: England & Wales 1996	7915
All recorded industry: UK 1996	8953

2.1.2.2 Non-anthropogenic sources

A quantity of ammonia emission from non-anthropogenic sources is by far lower than the emission from agricultural sources. The non- anthropogenic sources plays a small role in ammonia emissions, it contributes only a few percent to the total ammonia emission. Ammonia released to the atmosphere from different type of sources such as excrement of domestic or wild animals, microorganisms activity in soil, human sweat and breath, mobile sources, forest fires and slash burning [15].

2.2 Abatement of ammonia

2.2.1 Biofiltration

Biofiltration is one of widely used techniques in the industry for reduction of odorous gas including ammonia. In term of waste recycling as well as low construction and operating cost, it is considered as a suitable method for the removal of ammonia gas or any other odorous compounds. [18]. Biofiltration typically consists of a filter-bed of organic matter such as peat, wood chips, soil, compost, synthetic substances or their combination [18, 19]. In biofiltration process, microorganism cultures naturally grow biologically and cover bio solid host media in form of biofilm. When contaminants or odorous compounds pass through biologically enriched layer of the filter material, they are transferred to a developing biofilm and the microorganisms degrade or metabolize the contaminants to carbon dioxide and water or non-hazardous metabolic product [18]. In case of ammonia, it is absorbed onto biofilter packing materials due to its high H constant, forming ammonium ions on biofilm and bacteria changes ammonium ions to nitrites, producing H^+. The presence of H^+ predominant on biofilm reduces pH of the system and it increases the ability of biofilter to absorb more ammonia. The occurring nitrites are finally degraded to nitrate [20]. The basic biofiltration system for air pollution control is shown in Figure 2.3.
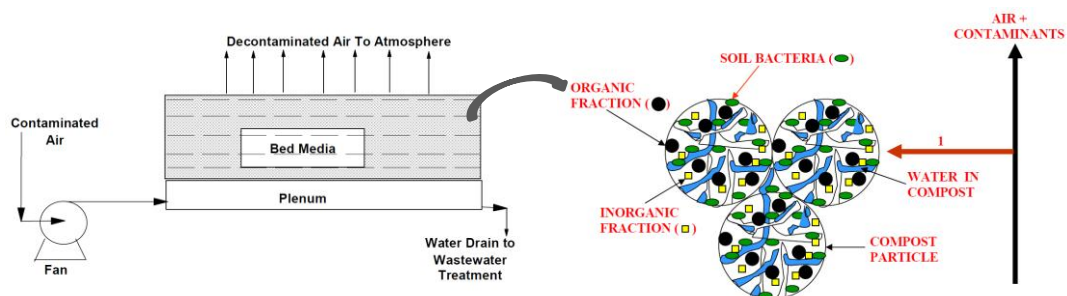
Figure 2.3 Basic biofiltration systems [19, 21]

2.2.2 Scrubbing

Scrubbing can be defined as odor controller device. The fundamental of scrubbing system is to use liquid, dry reagent or slurry to wash unwanted pollutants from a gas stream. The mechanism in scrubbing system depends on the target substance and sorbent but it mostly involves the inertial or diffusional impact, reaction of target substance with a sorbent or reagent slurry, or absorption into liquid solvent. In order to remove pollutant successively, the operation of system is generally performed in a two or three stages scrubber. The scrubber system has the advantage of handling high volume of air pollution but the drawback of this system is high investment and long resident time to reach the equilibrium [22]. Figure 2.4 shows the typical scrubbing system.
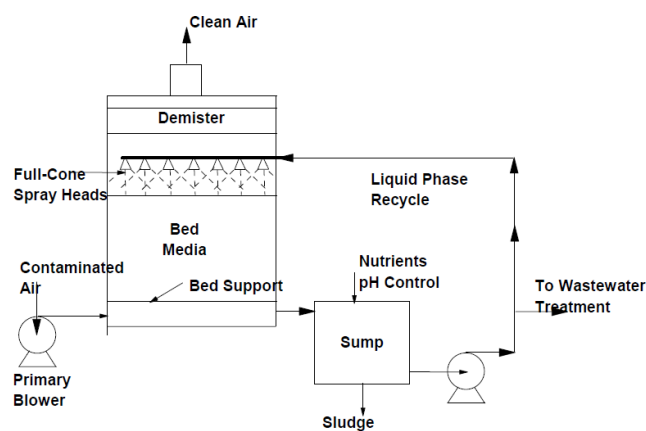
Figure 2.4 A typical scrubbing system [19]

2.3 Adsorption

2.3.1 Adsorption at gas-solid interface

Adsorption can be defined as the phenomena when a gas or liquid is exposing over a solid surface, they were bound and accumulated on the adsorbent by intermolecular forces. The density of gas or liquid is then appreciable enhanced on the particular solid interface. Generally, the adsorption efficiency is depending on the extent of the interfacial area between phases. From this reason, adsorbent should have a large specific surface area and highly porous nature or consist of fine particles [23]. In practical, the adsorption efficiency does not only depend on the physical properties of adsorbent materials mentioned previously but also depends on a chemical properties of adsorbent material such as chemical composition on adsorbent material, which can be selective to the particular adsorbate [24].

2.3.1.1 Physisorption of gases [23]

Physisorption is a phenomenon where substance physically adsorbs on the surface via van der Waals forces, which possesses a relatively low degree of specificity. Physisorbed molecule keeps its identity and on desorption, returns to the original phase form. The adsorbate molecule can excessively adsorb on surface or fill in micropore, mesopore or macropores of adsorbent material depending on adsobate size. The isotherm of gas adsorption on solid have a wide variety of forms, it is however classified into six groups in the IUPAC classification as shown in Figure 2.6.
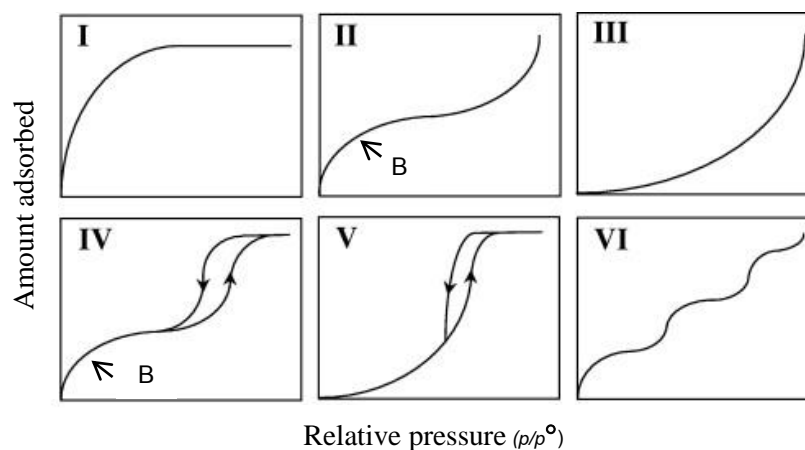
Figure 2.5 The IUPAC classification of physisorption isotherms [25].

Type I isotherm is concave to $p/p°$ axis, it rises sharply at low relative pressures and reaches a plateau, which means that the adsorbed amount by unit mass of solid approaches a limiting value as $p/p° \rightarrow 1$.

Type II isotherm is concave to $p/p°$ axis. It can be defined as the formation of an adsorbed layer whose thickness progressively increases when relative pressure is increased until $p/p° \rightarrow 1$. The pointed B represents the completion of the monolayer and the beginning of the multilayer formation.

Type III isotherm is convex to $p/p°$ axis, this type of isotherms are not the common type because it is indicative of weak interactions between adsorbate and adsorbent material.

Type IV isotherm, these type of isotherm is closely related to the type II isotherm. The hysteresis loop exhibits at two stages, the lower stage represents a progressive addition of gas on adsorbent whereas the upper stage shows the progressive withdrawal of gas from adsorbent material.

Type V isotherm is initially convex to the $p/p°$ axis. The exhibition of hysteresis loop involves the association of the pore filling and emptying mechanism on adsorbent material.

Type VI isotherm involves the layer-by-layer adsorption on highly uniform surface. The sharpness of the curve depends on the system and temperature.

2.3.1.2 Chemisorption of gases [23]

Chemisorption is defined as being the attraction of gas species to the solid surface via chemical interaction. The interaction between the adsorbate and adsorbent surface involves chemical bonds formation such as ionic or covalent bond that is irreversible reaction, which the chemisorbed molecules do not return to its original phase form.

Generally, a chemisorption isotherm exhibits a plateau at lower pressure than the pore filling plateau (physisorption isotherms). The adsorption is limited according to the completion of a chemically bound monolayer. A chemisorption isotherm of gas adsorption may refer as Langmuir isotherm, even if the mechanism involved may not fit into the Langmuir model assumptions but the Langmuir isotherm should not be used in the case of physisorption by porous solid. In certain case, it is quite difficult to obtain equilibrium data for chemisorption because the chemisorption reaction rate is very slow under certain conditions.

2.3.2 Breakthrough curve

Breakthrough curve represents the evolution of the target molecules concentration with respect to the contact time between gas/liquid and solid phase or sample volume in one period time [26]. Practically, breakthrough curves are employed as a tool to define and understand the characteristics of thermodynamic and kinetics of adsorption process, it is the most common basis for the evaluation of adsorbent behavior in a fixed-bed adsorption system. Breakthrough curves depend on operating conditions, bed geometry, heat effects, transport properties as well as equilibrium adsorption isotherm. The fundamental basis of the interpretation of breakthrough curve is the isotherm shape, which gives the information of the reaction kinetics, diffusion and dispersion behavior in the particular adsorption system. The characteristics of adsorbate adsorption on adsorbent in each condition however exhibits a unique isotherm shapes, it is due to the complexation with adsorbate or pore filling [27]. The typical breakthrough curve is shown in Figure 2.6.
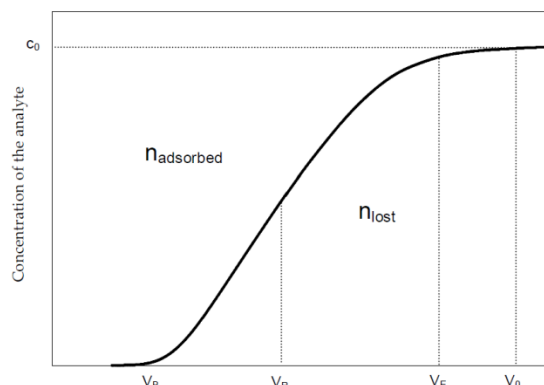
Figure 2.6 A typical breakthrough curve ($n_{adsorbed}$: the amount retained in column and n_{lost} : the amount lost)[26].

2.4 Adsorbent materials for gas applications

In gas adsorption system, the adsorbent materials are generally like those used in liquid system but the selection of adsorbent material for gas adsorption system is stricter. The most distinguish characteristics of adsorbent for gas and liquid application is the adsorbent particle size, which may affect the performance of adsorptive gas processes such as, pressure drop, volumetric capacity as well as mass transfer characteristics [23]. The most commonly used precursor size for producing commercial adsorbents for gas-phase applications is 1-2 mm [28].

2.4.1 Inorganic adsorbent materials

2.4.1.1 Silica gel [29, 30]

Silica gel is amorphous material assemble of microparticles of 2-20 nm in size to form of colloidal silica with pore size in the range 6-25 nm. Effective surface area of silica gel is in the range of 100-850 m^2/g depending on silica gel characteristics such as particle size and pore size. In most case silica gel is usually having a finer pore and larger surface area. The surface of silica gel consists of Si–OH and Si–O–Si groups, that have polar characteristics and it can be used to adsorb polar

compounds i.e. alcohols, phenols, ammines, water, etc. via hydrogen bonding mechanism. Typical properties of adsorbent-grade silica gel are shown in Table 2.3.

Table 2.3 Typical properties of adsorbent-grade silica gel [30]

	Physical properties
Surface area (m^2/g)	830
Density (kg/m^3)	720
Reactivation temperature (°C)	130-280
Pore volume (% of total)	50-55
Pore size (nm)	1-40
Pore volume (cm^3/g)	0.42
Adsorption properties	**Percent by weight**
H_2O capacity at 4.6 mm Hg, 25 °C	11
H_2O capacity at 17.5 mm Hg, 25 °C	35
O_2 capacity at 100 mm Hg, -183 °C	22
CO_2 capacity at 250 mm Hg, 25 °C	3
n-C_4 capacity at 250 mm Hg, 25 °C	17

2.4.1.2 Activated alumina [29, 30]

Activated alumina is a highly porous material produced from hydrated alumina with form of aluminium oxide with the formula $Al_2O_3 \cdot nH_2O$. It is in tan or white and has a chalk-like appearance, the surface is more polar than that of silica gel and has acidic characteristic. Surface area is in the range of 250- 350 m^2/g. At elevated temperature, activated alumina has a higher capacity for water adsorption than silica. Activated alumina is commonly used as desiccant and can be suitably used for hydrogen, helium, low molecular weight alkanes, chloride, fluoroalkanes, ammonia and sulfur dioxide applications.

2.4.1.3 Zeolites [29, 30]

Most zeolites are porous crystalline aluminosilicates, that are composed of SiO_4 and AlO_4 jointed together by sharing oxygen atoms. The appearances of zeolite are generally white, chalky and opaque. Zeolite has a crystalline form and exhibits high density of uniform dimension micropore within their internal structure. Having a high pore volume characteristic, zeolites are highly effective either for gas or liquid applications, separation of oxygen from air or separation of paraffins from naphtha, etc. The process of adsorption on zeolite depends on molecular shape and size or polarity of target substance.

2.4.2 Organic adsorbent materials

2.4.2.1 Activated carbon [29-31]

Activated carbon has long been known as a carbonaceous material of appreciable specific surface area, in general effective surface area ranges from 300 to 1500 m^2/g or it can exceed 3000 m^2/g for activated carbon produced from petroleum coke. Surface area of the produced activated carbon depends on based material, activation temperature, activating agent, etc. Activated carbon can be produced from a variety of carbon-rich material such as rice hull, wood, peat, coals, nutshells, coconut shells, pitches, coal tar, saran, recycle tires, sewage sludge and others. Generally, the processes of activated carbon manufacturing include gas activation and chemical activation. The gas activation is performed by first heating the raw material in the temperature range of 400-500 °C under inert gas condition to drive off volatile organic compounds and to form a small pore in carbon-based adsorbent materials. The carbonized material is then activated by gas stream such as CO_2 or flue gas at temperature range of 800-1000 °C. For the chemical activation, activated carbon can be produced by the introduction of zinc chloride or phosphoric acid directly to raw material but in this case the pores sizes are perhaps larger than the materials produce

from gas activation process. Typical pore sizes of activated carbon are shown in Table 2.4.

Application of activated carbon is more diverse than other adsorbent materials. It can be used either in gas or liquid purification such as odorous, colors, taste, decolorizing sugar solutions, VOC control, water treatment and hydrogen purification.

Table 2.4 Pore sizes in typical activated carbon [30]

	Micropores	**Mesopores**	**Macropores**
Diameter (nm)	< 2	2-50	> 50
Pore volume (cm^3/g)	0.15-0.5	0.02-0.1	0.2-0.5
Surface area (m^2/g)	100-1000	10-100	0.5-2

2.4.2.2 Polymer [29, 30]

Synthetic non-ionic polymeric adsorbents are mostly used in analytical chromatography applications. For industrial used, polystyrene/divinylbenzene copolymers, acrylic esters/divinylbenzene adsorbent are commercially available according to their wide variety of surface polarity and high pore volume. The effective surface area is usually smaller than activated carbon but may range up to750 m^2/g. Current applications of polymeric adsorbent material include decaffeination, purification of antibiotic as well as VOC recovery from off-gas. In practical, the applications of polymeric adsorbent materials are limited because the cost of polymeric adsorbent is typically high.

2.5 Sewage sludge-based adsorbent

Sewage sludge can be described as the biosolid residue generated during wastewater treatment activity. The constituents of sewage sludge are typically fats, urea, cellulose, and proteins [9]. Sewage sludge can be categorized as primary sludge

(1°), which is the material from primary settlement stage of wastewater treatment process; secondary sludge (2°) or activated sludge is the material obtained from the biological treatment of wastewater. In the last stage, dissolved nutrients and organic compounds are converted into bacterial cells and a larger amount of sludge is continuously produced.

Sewage sludge is one source of carbonaceous material. It can be transformed to adsorbent material such as activated carbon for gas and liquid applications [9].

2.5.1 Preparation of sewage sludge-based adsorbent materials

2.5.1.1 Adsorbents produced by carbonization

The raw sewage sludge can be used as starting material to produce the adsorbent by carbonization at 650-1000 °C. The specific surface area of carbonized sludge is generally maximized at high temperature, this is because volatile organic compound obscured on surface is evaporated at high temperature. Another aspect is that carbonization may result in the aromatization and dehydroxylation of the inorganic material and pore formation in carbonized sludge structure [9].

2.5.1.2 Adsorbents produced by physical activation

The production of sewage sludge adsorbent material by physical activation can be described as the burn-off the carbon fraction by gasifying gas such as CO_2, air, stream, air/N_2 or O_2/N_2 in the activation process at temperature in the range of 275-800 °C. This method can be performed by carbonization followed by physical activation. In this process, sewage sludge was first carbonized to release volatile organic matter and the obtained char is mixed with gasifying agent and subsequently carbonized again under inert gas atmosphere, in this stage a gasifying agent released from sewage sludge serving to activate the char. The mechanism of carbon produced by this method is however presently unknown [9].

2.5.1.3 Adsorbents produced by chemical activation

The principal of chemical activation is the introduction of chemical reagent to raw sewage sludge during activating process. There are wide varieties of chemical reagent available for sewage sludge-based adsorbent production such as KOH, $ZnCl_2$, H_2SO_4, H_3PO_4, NaOH, K_2S or the combination. The specific surface area of sludge increases after chemical activation process but the mechanism of the transformation of the organic or inorganic fraction in activated sludge was not entirely discernible, only few of them can be predicted such as $ZnCl_2$, H_3PO_4 and H_2SO_4. Since $ZnCl_2$, H_3PO_4 and H_2SO_4 is an acidic reagent, it increases material porosity by interacting with oxygen functional groups to catalyze the dehydration and dehydrogenation reactions, resulting in charring and aromatization of the carbon skeleton and hence the development in the pore structure [9].

2.6 Surface modification for gas removal

2.6.1 Physical modification

The physical properties of adsorbent material can be changed due to the physical modification. This approach is to improve the physical characteristic of adsorbent material such as specific surface area, pores volume as well as pore diameter, which can enhance the efficiency in removal of target substance [32]. One such method used to obtain the outstanding physical characteristic is whereby thermal treatment. In case of carbonaceous material, the thermal treatment not only improves material physical properties but also increases concentration of surface oxygen containing groups such as carbonyl oxygen atoms in esters, amides, carboxylic anhydrides, and oxygen atoms in hydroxyls or oxygen containing groups, which can interact with target substance and provides higher adsorption efficiency. The surface function groups existing on adsorbent material after thermal treatments are however, not a unique form, it depends on the nature of raw material [33].

2.6.2 Chemical modification

The chemical modification is one of the most effective methods for improving the adsorption efficiency of adsorbent material. It involves the introduction of chemical modifying agent onto adsorbent material to make the adsorbent surface more selective and favorable to the target substance [9], the specific application depends on the properties of the molecules to be adsorbed [34]. The chemical modification can be categorized as acidic or basic modification.

2.6.2.1 Acidic modification

Acidic modification is the introduction of acidic substance onto adsorbent material such as H_3PO_4, and H_2SO_4. The acidic groups on the adsorbent surface are introduced to the surface by different approaches depending on the application, but most case involves basic substance removal. The surface after modification can be composed of surface oxides such as carbonyl, carboxyl, phenolic hydroxyl, lactone and quinine groups, which increase the efficiency in adsorption of polar alkaline molecule, such as NH_3 [29].

2.6.2.2 Basic modification

One such method to improve the acidic substance uptake on adsorbent material is the introduction of a basic substance such as nitrogen-containing species onto adsorbent material. It has been reported that introduction of nitrogen-containing species by urea treatment changes the surface chemistry of adsorbent material; increases surface basicity and enhances SO_2 removal [33].

2.7 Literature review

The utilization of waste material has attracted more attention recently. There are many reports on adsorbent material development including the improvement of adsorption efficiency of adsorbents.

Regarding sewage sludge adsorbent materials, it is mostly used for the production of activated carbon for any other gas applications beside from NH_3 such as H_2S, SO_2 and VOC.

Chiang *et al*. [35] produced adsorbent material from aerobically and anaerobically digested sewage sludge for methyl ethyl ketone, toluene and trichloroethylene by pyrolysis method. They used various concentrations of $ZnCl_2$ solution (0. 1, 3, 5, 7 M) mixed with dry sewage sludge for 2 hours before pyrolysis. The pyrolysis was carried out in a fixed bed reactor under N_2 atmosphere, the temperature was controlled between 400-1000°C for 0.5, 1, and 2.0 h respectively. They found that, the optimum condition for manufacturing the adsorbent was to add 5M $ZnCl_2$ and heat the mixture at 550 °C for 1 h. The specific surface area of the adsorbent was increased with increasing $ZnCl_2$ concentration up to 5M and the maximum specific surface area for the aerobically and anaerobically digested sludge was approximately 585 m^2/g and 455 m^2/g, respectively.

Wen *et al*. [36] evaluated the adsorption capacity of activated carbon derived from sewage sludge for gaseous formaldehyde. They prepared sewage sludge-based adsorbent material by the combination of carbonization and impregnation method. The raw sewage sludge was first dried at 110 °C for 24 h and carbonized at 450 °C for 1.5 h under N_2 atmosphere. The sample was then impregnated with 6M $ZnCl_2$ solution at 85 °C for 5 h, the material was filtered and dried before activated at 750 °C for 2 h under N_2 atmosphere. The amount of formaldehyde adsorbed on the obtained activated carbon for formaldehyde was found to be 74.27 mg/g and 7.62 mg/g for formaldehyde concentration of 498 mg/m^3 and 0.41 mg/m^3, respectively.

Bagreev. *et al*. [37] studied the preparation of adsorbent material obtained from sewage sludge-derived fertilizer, Terrene by pyrolysis of sulfuric acid-treated granular fertilizer at 600, 800 or 950 °C. The adsorbents were prepared by mixing 30 g of Terrene with 10 mL of concentrated sulfuric acid, the resulting materials were

subsequently carbonized at 300 °C for 30 min. The obtained product was crushed and pyrolyzed at 600, 800, and 950 °C under N_2 atmosphere. The result showed that the activation with H_2SO_4 improved the material performance in H_2S removal with the combination of the specific chemistry of inorganic phase preserved on carbon material and the development of microporous structure where the surface reaction products can be stored. H_2S is converted to S, S^{2-} and SO_4^{2-} via the reaction with salts/oxides in an oxidizing atmosphere. The pores are gradually filled as the surface reactions precede. The H_2S removal occurs until all micropores are filled with the reaction/oxidation products.

Sharonov and Aristov [38] synthesized new composite of chlorides of alkaline-earth metals and porous alumina for ammonia adsorption. The commercial γ-Al_2O_3 was impregnated with aqueous solution of $MgCl_2$, $CaCl_2$ or $BaCl_2$ followed by drying at 300 °C. The sorption of ammonia was carried out in a fixed-bed cylindrical adsorber at 25-300 °C. It was found that the modification led to an increase in sorption capacity in the row $BaCl_2 < CaCl_2 < MgCl_2$ due to the interaction between salt and ammonia that resulted in the formation of ammonia complexes. The sorption capacity significantly decreased when the temperature increased. The sorption capacity of $MgCl_2$-porous alumina composite was found to be 58.6 and 11.6 mg/g at the temperature of 25 and 300 °C respectively, or 3.2 and 0.6 mole of ammonia per 1 mole of the salt supported on alumina.

Le Leuch. *et al*. [39] evaluated the activated carbons modified with aqueous solutions of Co(II) acetate, Cr(II) acetate and Fe(II) acetate as a media for reactive adsorption of ammonia. The commercial carbons were modified by incipient wetness impregnation and the process was completed by mixing the prepared solutions with activated carbons and shaking overnight. The samples were then stored in the oven at 110 °C. Then the oxidation of impregnated activated carbons was performed in a tube-type furnace. The process began at 25 °C and maintained at a constant rate of 5 °C per minute to the final temperature of 300 °C with 3 h holding time. The ammonia adsorptions were carried out at room temperature to evaluate the capacity of the sorbents for NH_3 removal at wet conditions. The results showed that the obtained activated carbons could remove ammonia and their capacity depended on the nature

of the metal deposit and its acidity. The capacity is also affected by the presence of moisture and surface functional groups and acidity. An introduction of metals/metal oxide onto the surface significantly enhanced the adsorption capacity. Reactive adsorption of ammonia took place via the formation of NH_4^+ ions as a result of (i) reaction with water and then the ammonium ion formed ammonium salt with deprotonated carboxylic functional group or (ii) reaction with hydroxyl group of acid functional group and the generated ammonium ion adsorbed on metal acidic site. Thus the removal process was governed by acid–base interactions.

Petit and Bandosz [40] prepared adsorbent from wood-based activated carbon modified with molybdenum and tungsten oxides for the removal of ammonia from air. The carbon samples were impregnated with solutions of ammonium metatungstate $((NH_4)_6H_2W_{12}O_{40})$ or ammonium molybdate $((NH_4)_6Mo_7O_{24}\cdot4H_2O)$. The samples were dried overnight at 120 °C and then heated at 500 °C for 3 h in a nitrogen atmosphere to remove ammonia and to form tungsten or molybdenum oxides. Adsorption capacity for ammonia removal was measured in dynamic conditions, at room temperature. The ammonia concentration was 1000 mg/L and the total flow rate of the inlet gas was 450 mL/min. The adsorbent bed contained granules of carbon, with a size between 1 and 2 mm, packed into a glass column. The ammonia concentration in the outlet gas was measured using an electrochemical sensor (Multi-Gas Monitor ITX system). The results showed that molybdenum and tungsten oxides distributed on the surface of activated carbon provided additional Brønsted centers for interactions with ammonia molecule or ammonium ions and consequently, enhanced ammonia uptake. The ammonia gas was adsorbed either via formation of ammonium salts with the deposited inorganic substance or via dissolution in water pre-adsorbed on solid surface.

As above mentioned research, sewage sludge-base adsorbents can be produced by carbonization and chemical modification/activation with various chemical reagents. Most of research reported the use of sewage sludge-based adsorbent for another gas application but the preparation of adsorbent from sewage sludge for ammonia gas removal has not been reported so far.

In this work, we are interested in producing adsorbent material from sewage sludge by carbonization combined with chemical modification that provides the specific active sites for ammonia gas removal.

CHAPTER III

EXPERIMENTAL

3.1   Instruments

The instruments used in this research are shown in Table 3.1

Table 3.1 List of instruments

Instruments	Manufacture: Model	Purpose
1. Flame atomic absorption spectrometer (FAAS)	Perkin Elmer: AAnalyst100	Determination of Zn on adsorbents
2. Thermogravimetric analyzer (TGA)	Perkin Elmer: Pyris1	Study of thermal stability of adsorbents
3. Surface area analyzer	BEL Japan: BELSORP-mini	Surface area determination
4. Scanning electron microscope	JOEL: JSM-5410 LV	Adsorbent surface analysis
5. Fourier transforms infrared spectrometer (FT-IR)	Nicolet: 6700	Functional group identification
6. Furnace	Carbolite	Adsorbents preparation
7. Homogenizer	Polytron : PT3100	Adsorbents preparation
8. Shaker	Janke & Kunkel: IKA_werk	Agitation of solution in titration experiments
9. Centrifuge	Sanyo: Centaur 2	Separation of adsorbents from solution
10. Stirrer	Gem: MS 101	Agitation of solution in titration experiments

3.2   Chemicals

All chemicals used in this research are listed in Table 3.2

Table 3.2 List of chemicals and supplier

Chemicals	Suppliers/Grade
Concentrated sulfuric acid, 95-97%	Merck/ for analysis
Ortho-phosphoric acid 85%	Merck/ for analysis
Concentrated nitric acid 65%	Aldrich/ for analysis
Concentrated hydrochloric acid 37%	Merck/ for analysis
Boric acid	Scharlau Chemie S.A./reagent grade
	Merck/ pro analysis
Zinc chloride	Carlo Erba Reagenti SpA/ for analysis
Sodium carbonate anhydrous	Fluka Chemie AG/ AR Grade
Sodium hydroxide	Merck/ for analysis
Potassium hydrogen phthalate	CARLO ERBA/ for analysis

3.3   Experimental procedures

3.3.1 Preparation of chemicals and reagents

Sulfuric acid solutions

Sulfuric acid solution (1, 3, 4, 5 or 6 M) was prepared by dilution of concentrated sulfuric acid solution (95-97%) with de-ionized water and used as a modifier for adsorbent modification.

Phosphoric acid solutions

Phosphoric acid solution (1, 3, 4, 5 or 6 M) was prepared by dilution of concentrated phosphoric acid (85%) with de-ionized water and used for adsorbent modification.

Zinc chloride solutions

Zinc chloride solution (1, 3, 4, 5 or 6 M) was prepared by dissolving the appropriate amount of $ZnCl_2$ in de-ionized water and used for adsorbent modification.

Hydrochloric acid solutions

Hydrochloric acid solutions (0.02, 0.05, 0.1 and 0.5 M) used for titration were prepared by dilution of the concentrated hydrochloric acid solution with de-ionized water. The desired solution was standardized with sodium carbonate solution (0.01, 0.025, 0.05 or 0.25 M) before use.

Boric acid solution

Boric acid solution (4% w/v) was prepared by dissolving the appropriate amount of H_3BO_3 in boiled de-ionized water and used for ammonia trapping.

Sodium hydroxide solutions

Sodium hydroxide solutions (0.1, 0.3 and 0.5 M) used for back titration of proton content in samples were prepared by dissolving the appropriate amount of NaOH in de-ionized water, the desired solution was standardized with sodium hydrogen phthalate solution, KHP (0.1, 0.3 or 0.5 M) before use.

Potassium hydrogen phthalate

Potassium hydrogen phthalate (KHP) solutions (0.1, 0.3 and 0.5 M) were prepared by dissolving the appropriate amount of KHP in de-ionized water and used for standardization of sodium hydroxide solutions.

Sodium carbonate solutions

Sodium carbonate solutions (0.01, 0.025, 0.1 and 0.2 M) were prepared by dissolving the appropriate amount of Na_2CO_3 in de-ionized water and used for standardization of hydrochloric acid solutions.

3.3.2 Preparation of sewage sludge-based adsorbent

The sewage sludge was collected from Dindang municipal wastewater treatment plant, Bangkok, and first sun-dried for 1 week, then crushed and sieved to particle size of 1-2 mm. The obtained sewage sludge was kept at room temperature until use.

3.3.2.1 Effect of carbonization temperature

Dried sewage sludge was carbonized at 300 or 500 °C in air atmosphere for 2 h and sieved to a particle size of 1-2 mm before use. Both non-carbonized and carbonized sewage sludge were modified with modifying agents and their adsorption properties were evaluated and compared.

3.3.2.2 Effect of impregnation time

Non-carbonized and carbonized sewage sludge was chemically modified by impregnation with 5M of H_2SO_4, H_3PO_4 or $ZnCl_2$ for 3 and 24 hours. To evaluate the effect of impregnation time, the H^+ content or amount of Zn on adsorbents prepared by using impregnation time of 3 and 24 hours was determined and compared.

3.3.2.3 Effect of concentration of the modifying agent

In this experiment, the effect of modifying agent concentration was studied so as to determine the suitable concentration for the optimum loading of modifying agent on adsorbent material. The variable concentrations of modifying agent were used to modify the surface of adsorbent material. A portion of 11 g of sewage sludge carbonized at 500 °C was each modified with H_2SO_4, H_3PO_4 or $ZnCl_2$ of concentration of 1, 3, 4, 5 or 6 M at room temperature for 3 h using homogenizer machine (POLYTRON3100). The resulting products were subsequently filtered and dried at 120 °C overnight. The prepared adsorbent was kept in a desiccator until used.

3.4   Adsorbents characterization

The physical properties of adsorbents were characterized by BET, SEM and TGA technique to investigate surface area, surface morphology and thermal stability of material, respectively. FT-IR was used to identify the funtional group on adsorbent material before and after ammonia gas exposure. The chemical properties of adsorbent modified with H_2SO_4 and H_3PO_4 were characterized by titration method to determine H^+ content immobilized on adsorbent surface and flame atomic adsorption spectrometer was used to determine the amount of Zn immobilized on adsorbent surface.

3.4.1 Nitrogen adsorption (Brunauer-Emmett-Teller method (BET))

The specific surface area (S_{BET}) of non-modified and modified non-carbonized sewage sludge and sewage sludge carbonized at 300 or 500 °C were determined by nitrogen adsorption-desorption isotherms measured at 77 K using a Belsorp-mini analyzer. Surface area of the samples was calculated by fitting the isotherm with the BET model. The samples was weighted about 40 mg for pretreatment at 150°C for 2 hours before surface area measurement, then the pretreated sample was weighted exactly for nitrogen adsorption experiment.

3.4.2 Thermogravimetric analysis (TGA)

Thermal stability of non-carbonized sewage sludge and sewage sludge carbonized at 300 or 500 °C were determined by thermogravimetric analysis. TGA was performed on a Perkin Elmer (Pyris1), the temperature increased from 30-800°C under nitrogen atmosphere at a constant heating rate of 10 °C/min.

3.4.3 Scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (SEM/EDX)

SEM generates a signal on solid surface by the interaction of a high energy electron beam with atoms in sample. It was used to exhibit the external morphology of adsorbent surface. The chemical composition of sample surface was obtained from SEM/EDX technique. The X-ray excitation energy interacts with sample producing signal that contains information about the elemental composition on the sample external surface.

3.4.4 Fourier-transform infrared spectrometry (FT-IR)

FT-IR was used to identify the characteristic functional group of adsorbent material. Infrared spectra were recorded within the wavenumber range of 400-4000 cm^{-1} using the transmittance mode with 4 scans with the wave number resolution of ± 4 cm^{-1} by KBr pellet technique.

3.4.5 Determination of acid content by acid-base titration method

The acid content on adsorbents surface modified with H_2SO_4 and H_3PO_4 were determined by back titration method. A portion of 50 mg adsorbent was placed into a plastic test tube and 10 mL of NaOH solution (0.1, 0.3 or 0.5 M) was subsequently added. The mixtures were shaken for 24 hours. The excess base was titrated with HCl solution (0.02, 0.05, or 0.1 M). The acid content is reported as number of H+ equivalents per gram adsorbent.

3.4.6 Flame atomic adsorption spectroscopy

To determine the amount of Zn on surface, a portion of 50 mg adsorbent was added into the mixture of HCl and HNO_3 solution in a volume ratio of 3:1, respectively. The mixture was shaken for 24 h and the amount of Zn^{2+} dissolved in solution was further determined by a flame atomic absorption spectrometer.

3.5   Adsorption of ammonia gas

The ammonia adsorption system is shown in Figure 3.1.
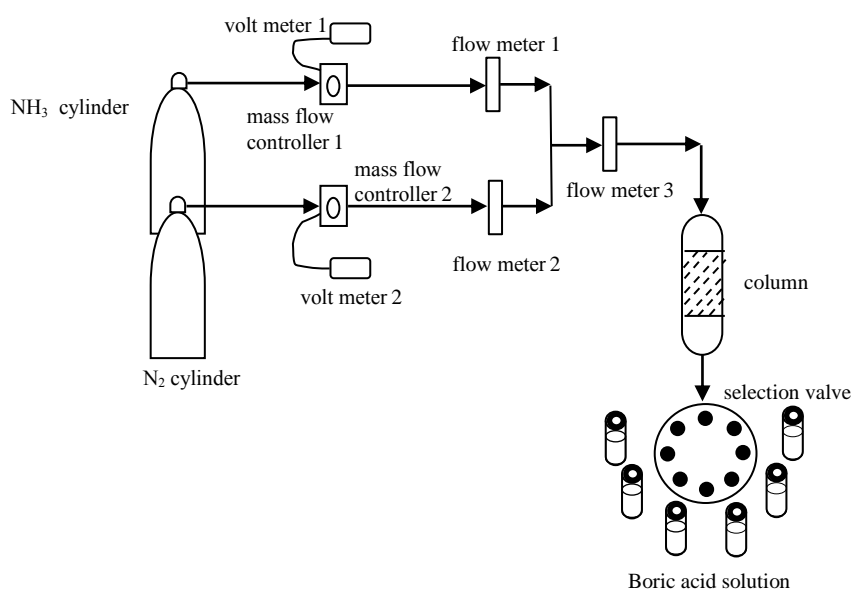
Figure 3.1 Ammonia adsorption system (mass flow controller 1: NH_3 flow rate 25 mL/min, mass flow controller 2: N_2 flow rate 95 mL/min, flow meter 1: NH_3 flow rate 5 mL/min, flow meter 2: N_2 flow rate 50 or 70 mL/min, flow meter 3: flow rate of NH_3 and N_2 mixing gas 30 mL/min.)

Ammonia adsorption was carried out in a fixed bed reactor. Two sizes of glass column (Figure 3.3) were used to evaluate the adsorption behavior and column capacity. The sizes of glass column are 5 cm length with diameter of 1 cm (bed volume 3.93 cm^3) and 20 cm length with diameter 1 cm (bed volume 15.71 cm^3). A portion of NH_3 gas from column outlet was collected every minute using control

selection valve operated by Hyper terminal program connected to the computer, a portion of NH_3 from column outlet was first run to the selection valve port 1 and automatically move from port 2-8 every minute during collecting process. The selection valve port 2-8 was directly connected to Teflon tube, which steep in 30 mL 4% boric acid solution and a portion of NH_3 was then trapped into a boric acid solution. The manifold of selection valve is shown in Figure 3.2.
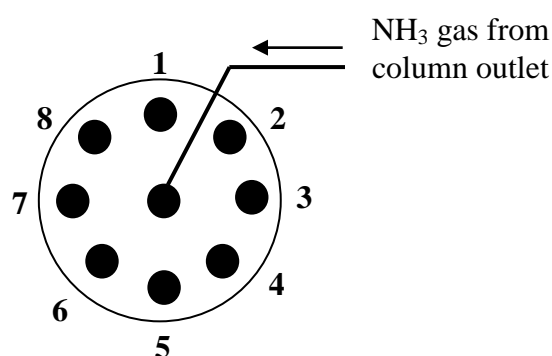
Figure 3.2 Selection valve manifold
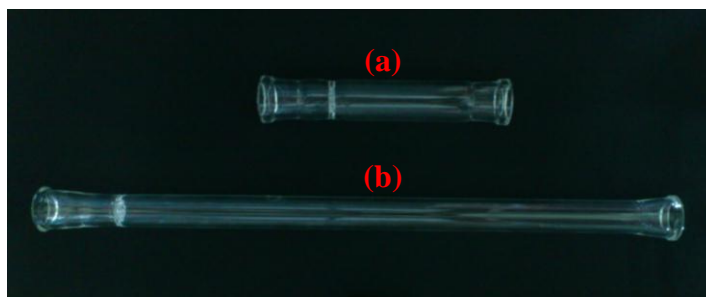
Figure 3.3 Glass column (a) 5 cm length, 1 cm i.d. and (b) 20 cm length, 1 cm i.d.

To study the adsorption of ammonia, a portion of 3 g adsorbent was placed into a glass column of 5 cm length with diameter of 1 cm or 9 g adsorbent was placed into a glass column of 20 cm length with diameter 1 cm. The mixture of N_2 and NH_3 gas was passed through the packed column continuously with a flow of 30 mL/min. The outlet gas from the column was bubbled into 30 mL boric acid solution (4% w/v). The titration method was used to determine ammonia concentration in the gas mixture

[41]. When ammonia gas dissolved in boric acid solution (H_3BO_3), it will react with H_3BO_3 to form $NH_4H_2BO_3$ (equation (1)). The amount of occurring $NH_4H_2BO_3$ was titrated with 0.05 mol/L HCl solution using methyl orange as indicator, the reaction of and HCl is shown in equation (2). At the end point, the solution color turned from yellow to orange. In this study, adsorption capacities of the adsorbent and breakthrough curve were observed.

$$H_3BO_3(l) + NH_3(g) \longrightarrow NH_4H_2BO_3(l) \tag{1}$$
$$NH_4H_2BO_3(l) + HCl(l) \longrightarrow H_3BO_3(l) + NH_4Cl(l) \tag{2}$$

3.5.1 Breakthrough curve

Breakthrough curve represented ammonia concentration in gas sample after column adsorption in function of adsorption time. It was plotted between C/C_0 and time, where C is the concentration of ammonia at column outlet at a given time and C_0 is the initial concentration of ammonia. Breakthrough curve was observed from ammonia adsorption study. The initial ammonia concentration was regulated to the desired concentration each time of adsorption study.

3.5.2 Effect of initial ammonia concentration

The effect of initial ammonia concentration on adsorption efficiency was studied by varying the nitrogen flow at 50 and 70 mL/min while the ammonia gas flow rate was fixed at 5 mL/min. Nitrogen gas flow rate affected the initial concentration of ammonia in gas mixture that flowed through the column at one period time, the adsorption capacity and breakthrough curve characteristic of each flow of N_2 was compared.

CHAPTER IV

RESULTS AND DISCUSSION

In this chapter, the results are divided into two sections. The first section involves the preparation of adsorbent material from non-carbonized sewage sludge (SW-NC), sewage sludge carbonized at 300 °C (SW-C300) and 500 °C (SW-C500) using surface modification method to obtain reactive surface for ammonia gas removal. The surface modification relied on the impregnation of H_2SO_4, H_3PO_4 and $ZnCl_2$ solution onto sewage sludge materials. The non-carbonized sewage sludge adsorbents obtained after surface modification with H_2SO_4, H_3PO_4 and $ZnCl_2$ refer to SW-NC-S, SW-NC-P and SW-NC-Z, respectively. The sewage sludge carbonized at 300 °C and modified with H_2SO_4, H_3PO_4 and $ZnCl_2$ are named SW-C300-S, SW-C300-P and SW-C300-Z, respectively, while sewage sludge carbonized at 500 °C and modified with these agents are called SW-C500-S, SW-C500-P and SW-C500-Z, respectively.

The final section focuses on the study of the effect of parameter that may affect the adsorption efficiency of adsorbent material including the effect of initial ammonia concentration and column size.

4.1 Preparation of sewage sludge-based adsorbent

The starting material used in this experiment was discarded sewage sludge originated from Dindang municipal wastewater treatment plant. The material had a mud like appearance, blackish brown color, and unfavorable smell. To obtain dried sewage sludge, the material was first sun-dried, then crushed and sieved to a particle size of 1-2 mm, which is the commonly used size of adsorbents for gas adsorption. The resulting materials were carbonized at 300 or 500 °C in air atmosphere for 2 h. The carbonized samples appeared as black solids, were sieved again to ensure that the particle size was in the range of 1-2 mm. To improve the efficiency in ammonia adsorption, the materials were chemically modified with 1, 3, 4, 5 and 6 M of H_2SO_4,

H$_3$PO$_4$ or ZnCl$_2$ solution at room temperature for 3 h using homogenizer machine (POLYTRON3100). The resulting products were subsequently filtered and dried at 120 °C overnight. The effect of carbonization temperature and modifying agent concentration were further investigated. The steps of adsorbent preparation are shown in scheme 4.1.
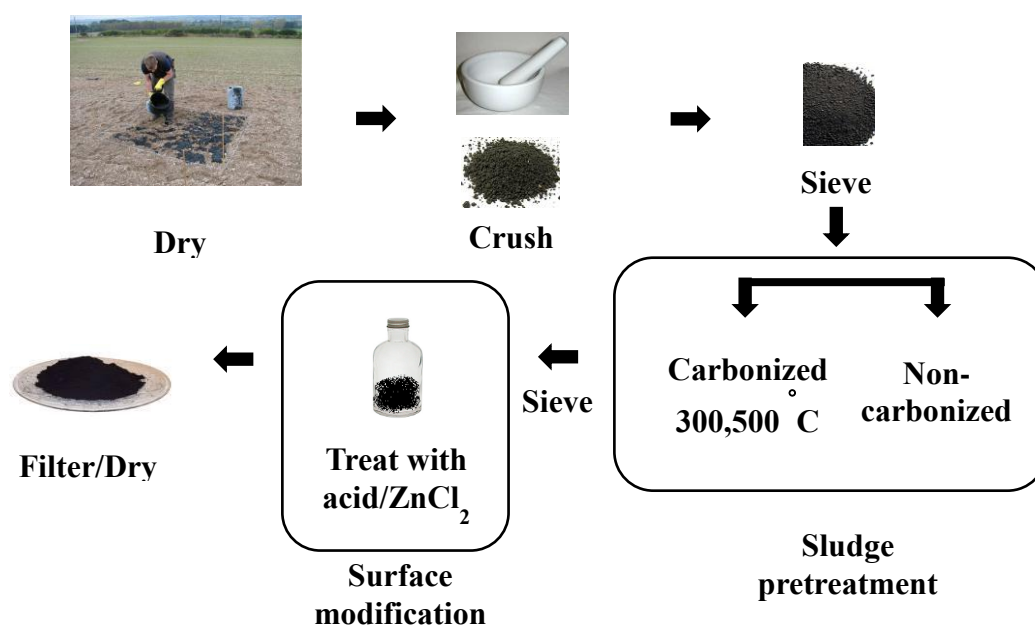
Scheme 4.1 The steps of adsorbent preparation.

4.1.1 Effect of carbonization temperature

Since the sewage sludge carbonization was carried out under air atmosphere, yield of the adsorbent strongly depended on the carbonization temperature as shown in Table 4.1. When the sludge was carbonized at 300°C, yield of obtained material decreased due to the partial loss of volatile organic matter in sewage sludge which was mostly removed at 500°C. Moreover, some of sewage sludge carbonized at 500 °C in the presence of oxygen turned into ash, which also brought a lower yield in this condition.

Table 4.1 Percent yield and percent ash of SW-NC, SW-C300 and SW-C500

Adsorbent	Yield (%)*	Ash (%)*
SW-C300	71.94 ± 0.5	0.00
SW-C500	57.16 ± 0.36	0.79 ± 0.65

* Mean ± S.D. (n=3)

To investigate the effect of carbonization temperature on the physical properties and surface morphology of sewage sludge, the carbonized sludge were characterized and the results are shown in the following part.

4.1.1.1 Surface area analysis

Results from surface area analysis of SW-NC, S.W-C300 and SW-C500 are shown in Table 4.2.

Table 4.2 Surface area analysis of SW-NC, SW-C300 and SW-C500

Adsorbent	surface area (m^2/g) *	SD
SW-NC	0.19 - 2.37	1.50
SW-C300	4.01 - 5.11	0.60
SW-C500	52.10 - 59.40	3.95

* (n=3)

The surface area of the obtained adsorbent depends on the carbonization temperature used, as carbonization temperature increased, the adsorbent surface area significantly increased. Considering the surface area of SW-NC and SW-C300, there was only a slight increase in specific surface area. It is probably because the volatile organic matter still remained in SW-C300 material. On the other hand, the specific surface area of the adsorbent was obviously increased when carbonization temperature increased to 500 °C due to the vaporization of volatile organic compound

from adsorbent surface. These results correspond to the information in previous part that showed a remarkable decrease in percent yield of material when carbonization temperature increased up to 500 °C.

4.1.1.2 Thermogravimetric analysis

Proximate analysis of sewage sludge constituents was performed using thermogravimetric analysis (TGA) on a Perkin Elmer (Pyris1). The temperature was increased under nitrogen atmosphere from 30-800 °C at a constant heating rate of 10 °C/min. Figure 4.1 shows TGA curve of SW-NC, SW-C300 and SW-C500. The TGA curve of SW-NC and SW-C300 show the initial weight loss of 50.77 % at the temperature range of 200 to 500 °C for SW-NC and 25.50 % at the temperature range of 350 to 500 °C for SW-C300. The results indicate that both of SW-NC and SW-C300 was composed of volatile organic compounds, which can be vaporized at the temperature range of 200 to 500 °C. In case of SW-C500, the TGA profile shows a slight weight loss of about 12%, mainly due to moisture content. It was inferred that the volatile organic compounds were not left in SW-C500 but the main composition was carbon in the material. Furthermore, percent fixed carbon increased when carbonization temperature increased. Percent of fixed carbon in SW-NC, SW-C300 and SW-C500 was found to be 55, 75 and 88 % respectively.
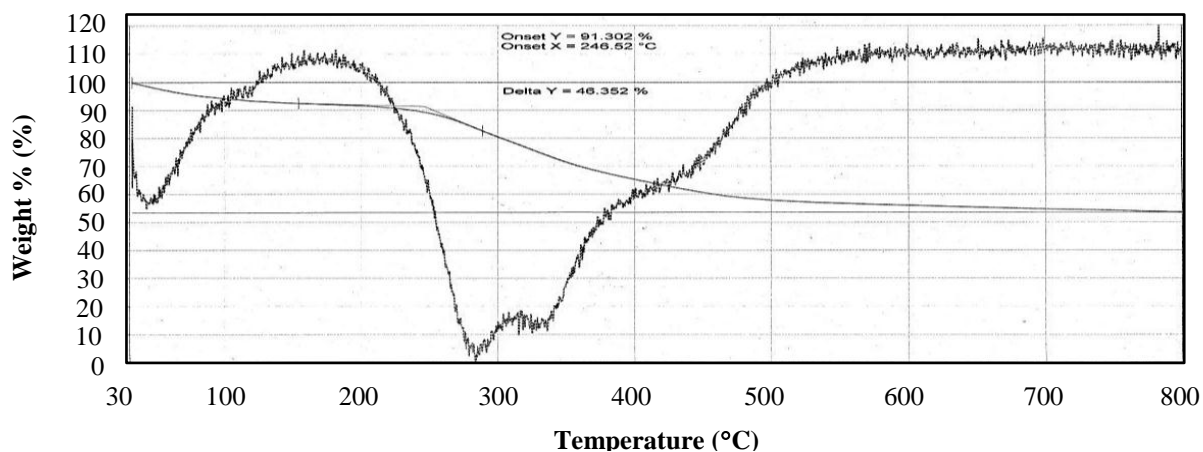
(a)
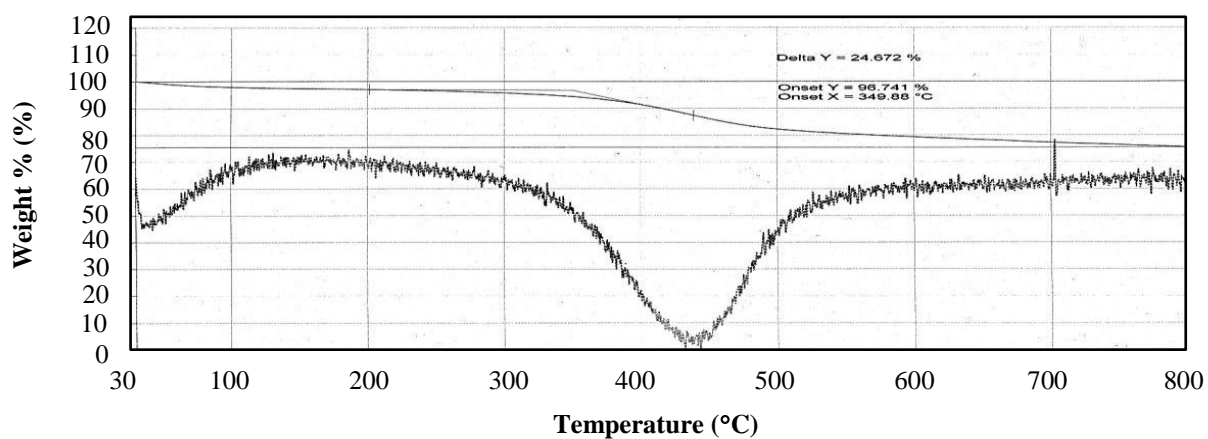
(b)
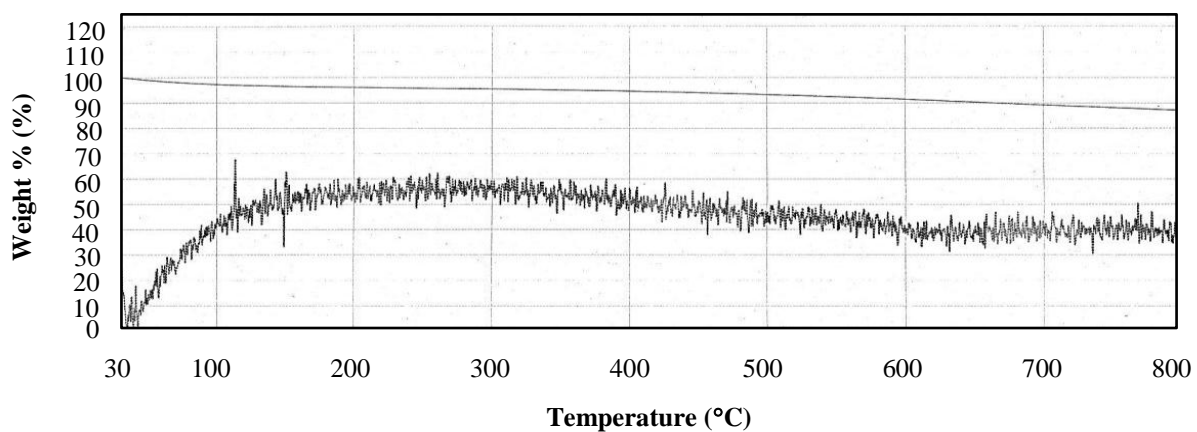
(c)

Figure 4.1 TGA curves of (a) SW-NC, (b) SW-C300 and (c) SW-C500.

4.1.1.3 SEM images of SW-NC, SW-C300 and SW-C500

Scanning electron microscope (SEM) was directed towards a morphological characterization of adsorbent materials undergone with different treatment condition. Figure 4.2 shows SEM image of SW-NC, SW-C300 and SW-C500, respectively. Considering the surface morphology of SW-NC, the outer surface of material was very dense and smooth, and it became loosen after carbonization according to the vaporization of volatile organic compounds. For SW-C300, the surface morphology exhibited rough surface with various distinct level of surface and after carbonization at 500 °C, it is obviously seen that a predominately of roughness character occurred on adsorbent surface. The change of surface morphology after carbonization may result in an increase in surface area of the obtained absorbents as observed previously.

(a)　　　　　　　　　(b)　　　　　　　　　(c)
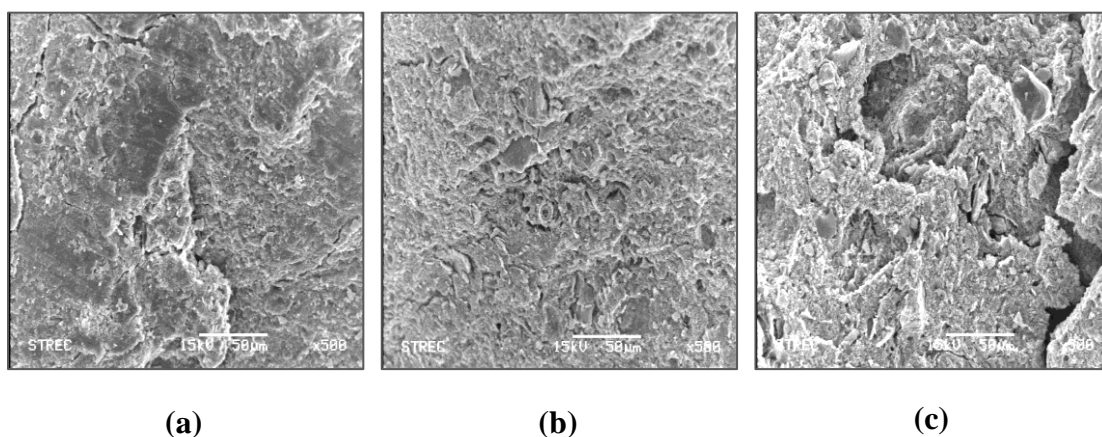
Figure 4.2 SEM images of (a) SW-NC, (b) SW-C300 and (c) SW-C500 at 500 magnifications.

4.1.1.4 Impregnation and comparison of adsorption efficiency of the modified carbonized and non-carbonized SW

In order to study the effect of carbonization temperature on the adsorption efficiency of the desired final products, the non-carbonized and carbonized sludge were further modified with H_2SO_4, H_3PO_4 and $ZnCl_2$. The modifying agent solution of 5 M was chosen as a model solution. Since H_2SO_4, H_3PO_4 and $ZnCl_2$ have their own distinctive properties and it would affect the adsorption behavior differently, therefore, it is necessarily to investigate and evaluate the performance of the adsorbents modified by these agents separately. In this experiment, the starting materials were impregnated with the modifying agent solution for 3 hours and the resulting adsorbents were further used in the ammonia adsorption..

The material SW-NC modified with 5M of H_2SO_4, H_3PO_4 and $ZnCl_2$ refer to SW-NC-S5, SW-NC-P5 and SW-NC-Z5, respectively whereas SW-C300 modified with 5M of H_2SO_4, H_3PO_4 and $ZnCl_2$ refer to SW-C300-S5, SW-C300-P5 and SW-C300-Z5 respectively and SW-C500 modified with 5M of H_2SO_4, H_3PO_4 and $ZnCl_2$ refer to SW-C500, SW-C500-P5 and SW-C500-Z5 respectively. To evaluate the success in impregnation, the surface acidity of adsorbents modified with H_2SO_4 and H_3PO_4 were determined by the back titration method and the amount of Zn by flame atomic absorption spectrometry. Table 4.3 shows the proton content on adsorbents modified with H_2SO_4 and H_3PO_4 and the amount of Zn immobilized on surface, respectively.

Table 4.3 Proton and Zn content on adsorbent modified with 5 M of H_2SO_4, H_3PO_4 and $ZnCl_2$

Adsorbents	H^+ contents*,[a] (mEq)	Zn contents* (mmol)
SW-NC	1.88 ± 0.26	0.02
SW-NC-P5	7.53 ± 0.10	-
SW-NC-S5	10.96 ± 0.14	-
SW-NC-Z5		2.27 ± 0.01
SW-C300	1.94 ± 0.46	0.03
SW-C300-P5	3.19 ± 0.05	-
SW-C300-S5	7.69 ± 0.37	-
SW-C300-Z5	-	0.37
SW-C500	0.96 ± 0.30	0.03
SW-C500-P5	5.25 ± 0.15	-
SW-C500-S5	8.34 ± 0.15	-
SW-C500-Z5	-	1.80 ± 0.08

* Mean ± S.D. (n=3)

[a] Eq stands for equivalent.

It is obviously seen that the H^+ and Zn content on modified adsorbents is larger than that observed on the non-modified, indicating that H_3PO_4, H_2SO_4 and $ZnCl_2$ were successfully immobilized onto the surface of sewage sludge adsorbent materials. The H^+ or Zn content immobilized on SW-NC was found to be higher than those on SW-C300 and SW-C500. Regarding the results obtained from TGA and SEM, the SW-NC material was composed of high content of volatile organic matter with the surface where the physisorption of the modifying agent was more favorable, compared to SW-C300 and SW-C500 surface that contained less organic matter. On the other hand, SW-C500 composed mainly of fixed carbon, had a greater surface area, allowing the adsorption of modifying agents to occur through the hollow of surface. Regarding modified SW-C300, the H^+ and Zn contents found are the lowest

of all materials probably due to a low content of volatile organic matter and low surface area.

Breakthrough curve of ammonia adsorption by column containing SW-NC, SW-C300 and SW-C500 modified with 5M of H_3PO_4, H_2SO_4 and $ZnCl_2$ are shown in Figure 4.3, 4.4 and 4.5 respectively. Column efficiency is related to the efficiency in ammonia adsorption by adsorbent and hence determined in term of amount of ammonia adsorbed per unit mass of adsorbent (mg/g) (Table 4.4).

Figure 4.3 Breakthrough curve of ammonia adsorption by SW-NC-P5 (C_0 18.20 mmol/L), SW-C300-P5 (C_0 18.56 mmol/L) and SW-C500-P5 (C_0 21.02 mmol/L); adsorbent 3 g and gas flow rate 30 mL/min.

Figure 4.4 Breakthrough curve of ammonia adsorption by SW-NC-S5 (C_0 19.39 mmol/L), SW-C300-S5 (C_0 19.69 mmol/L) and SW-C500-S5 (C_0 19.05 mmol/L); adsorbent 3 g and gas flow rate 30 mL/min.

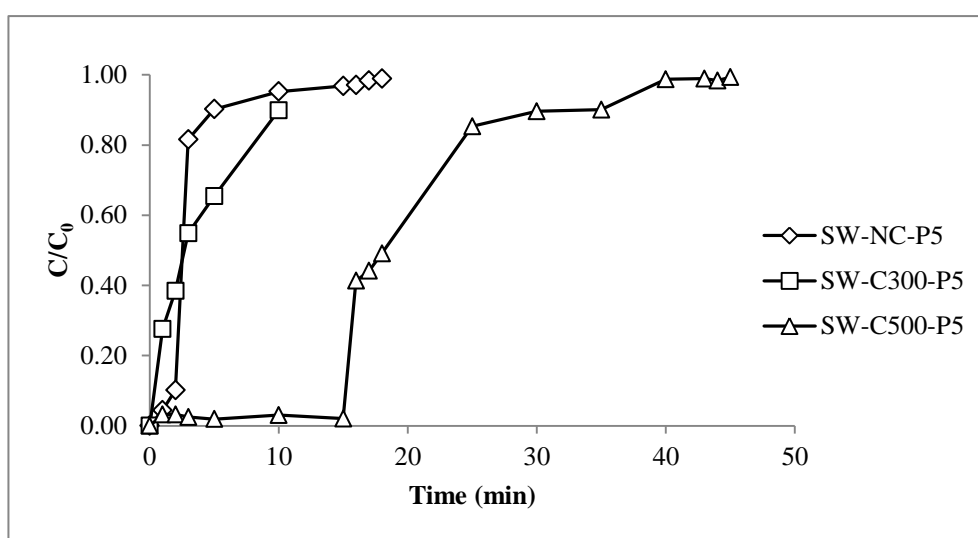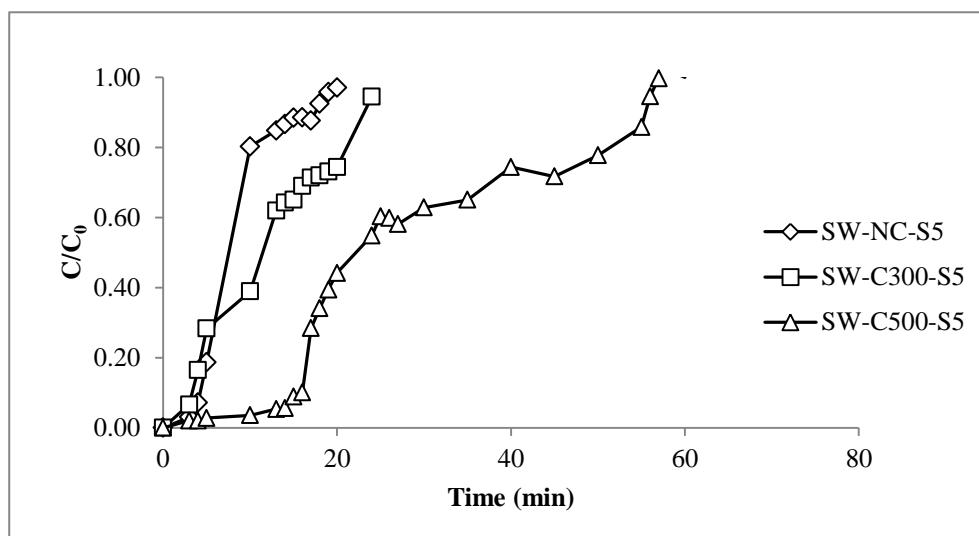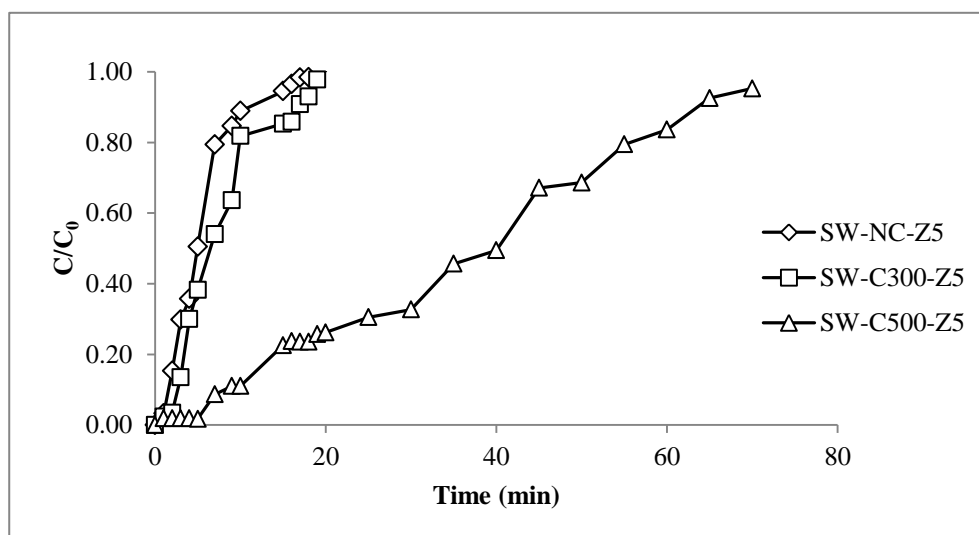**Figure 4.5** Breakthrough curve of ammonia adsorption by SW-NC-Z5 (C_0 18.45 mmol/L), SW-C300-Z5 (C_0 19.38 mmol/L) and SW-C500-Z5 (C_0 20.08 mmol/L); adsorbent 3 g and gas flow rate 30 mL/min.

Table 4.4 Column efficiency in ammonia adsorption by of SW-NC, SW-C300 and SW-C500

Adsorbent	Column efficiency* (mg/g)
SW-NC-P5	46.89 ± 2.32
SW-NC-S5	39.67 ± 2.22
SW-NC-Z5	40.42 ± 2.63
SW-C300-P5	46.08 ± 0.54
SW-C300-S5	52.66 ± 1.67
SW-C300-Z5	43.27 ± 1.52
SW-C500-P5	93.43 ± 5.98
SW-C500-S5	101.78 ± 3.26
SW-C500-Z5	132.94 ± 2.42

*Mean$\pm$ S.D. (n=3)

According to the results from Figures 4.3-4.5 and Table 4.4, the adsorption behavior of SW-NC and SW-C300 modified with 5M of H_3PO_4, H_2SO_4 and $ZnCl_2$ were not much different. As shown previously, the SW-NC contained a high density of chemical active sites but it shows relatively low adsorption efficiency. It is likely that H^+ and Zn found in SW-NC might not be solely immobilized on outer surface where ammonia can freely access through. The ammonia adsorption efficiency of SW-C300 was also low due to a low number of chemical active site. On the other hand, the adsorbents obtained from SW-C500 provided the best results in ammonia adsorption of all materials according to a high extent of H^+ and Zn occupied on surface and available for ammonia adsorption. Thus, SW-C500 is recommended for the subsequent study.

In an attempt to improve the efficiency in impregnation of modifying agents on SW-C500, the impregnation time of 24 hours was adopted for the modification with 5 M H_2SO_4, H_3PO_4 and $ZnCl_2$. After 24 hours of shaking, the yield of particles of desired size (1-2 mm) was very low because adsorbent particles were shattered

during the preparation process. In addition, H^+ or Zn content on SW-C500 modified at the impregnation time of 24 hours was not much higher than those of 3 hours (Table 4.5).

Table 4.5 Proton and Zn content on adsorbent modified with 5 M of H_2SO_4, H_3PO_4 and $ZnCl_2$ solution at 3 and 24 h

Adsorbent	3 h impregnation		24 h impregnation	
	H^+ content (mEq)	Zn content (mmol)	H^+ content (mEq)	Zn content (mmol)
SW-C500-P5	5.25 ± 0.15	-	9.36 ± 1.04	-
SW-C500-S5	8.34 ± 0.15	-	10.42 ± 0.08	-
SW-C500-Z5	-	1.80 ± 0.08	-	1.58 ± 0.03

Mean ± S.D. (n=3)

Eq stands for equivalent.

The surface modification was thought to occur via the physical adsorption of modifying agents on the sewage sludge. Therefore, the adsorption equilibrium would be reached in a certain interval of time. It is likely that the adsorption equilibrium was reached before 24 hour of impregnation; an increase in impregnation time to 24 hours will not result in a notably higher adsorbed amount of modifying agent. From an economic point of view, the impregnation time of 24 hours has the disadvantages of time and energy consuming, which leads to the higher cost of operating systems. Hence, the impregnation time of 24 hours was not recommended and impregnation time of 3 hours was chosen for subsequence experiments.

4.1.2 Effect of modifying agent concentration

This experiment aims to evaluate the effect of modifying agent concentration on the ammonia adsorption efficiency of modified SW-C500 and find the suitable modifying agent concentration for adsorbent preparation. The modifying agent concentrations used in this work were 1, 3, 4, 5 and 6 M. The chemical properties of sewage sludge carbonized at 500 °C modified with 1, 3, 4, 5 and 6 M of H_3PO_4, H_2SO_4 and $ZnCl_2$ are shown in Table 4.6. The adsorbents prepared by using modifying agent of 1-6 M concentration are given the names with the concentration as SW-C500-P1, SW-C500-P3, SW-C500-P4, SW-C500-P5, SW-C500-P6, SW-C500-S1, SW-C500-S3, SW-C500-S4, SW-C500-S5, SW-C500-S6, SW-C500-Z1, SW-C500-Z3, SW-C500-Z4 and SW-C500-Z5.

According to the results in Table 4.6, H^+ and Zn content on modified SW-C500 increased when the concentration of modifying agent solution was raised. On the other hand, the best modification efficiency was achieved in the case of using modifying agent at 1 M concentration. The modification efficiency decreased rapidly in the modification with 3 M and gradually changed thereafter. This phenomenon is explained by the limited surface of SW-C500. An increase in modifying agent concentration to higher than 3 M would not lead to a dramatic change in modifying extent on solid phase, and on the contrary, higher amount of modifying agent was left in solution.

It should be noted that H^+ content on surface of SW-C500-S were higher than that observed on SW-C500-P. It is because H_2SO_4 which is a strong acid generates H^+ in higher amount than weak acid H_3PO_4 when they are used in the same concentration. For the adsorbent modified with $ZnCl_2$ solution, the amount of Zn on surface was slightly low.

Table 4.6 Proton and Zn content on SW-C500 modified with 1, 3, 4, 5 and 6 M of H_2SO_4 and H_3PO_4 and $ZnCl_2$ solution

Adsorbent	H^+ content (mEq) [a]	Zn content (mmol/g) [a]	Modification efficiency [b] (%)
SW-C500	0.96 ± 0.3	0.03	
SW-C500-P1	2.85 ± 0.23		2.10
SW-C500-P3	3.96 ± 0.16		1.10
SW-C500-P4	4.54 ± 0.36		0.99
SW-C500-P5	5.25 ± 0.15		0.95
SW-C500-P6	5.99 ± 0.80		0.93
SW-C500-S1	6.75 ± 0.17		9.65
SW-C500-S3	7.28 ± 0.43		3.51
SW-C500-S4	7.58 ± 0.54		2.76
SW-C500-S5	8.34 ± 0.15		2.46
SW-C500-S6	6.89 ± 0.55		1.65
SW-C500-Z1		0.65 ± 0.04	1.97
SW-C500-Z3		1.33 ± 0.01	1.41
SW-C500-Z4		1.60 ± 0.04	1.28
SW-C500-Z5		1.79 ± 0.08	1.15
SW-C500-Z6		1.97 ± 0.04	1.06

Eq stands for equivalent

[a] Mean $\pm$ S.D. (n=3)

[b] % modification $= \frac{Eq\ H^+_{mod}}{Eq\ H^+_{tot}} \times 100$, where Eq H^+_{mod} is number of H^+ equivalents modified on adsorbent, Eq H^+_{tot} is number of total H^+ equivalents in modifying agent solution.

4.1.2.1. Physical properties

Surface area analysis

Nitrogen adsorption and BET method were used as a tool to clarify the physical property of adsorbent in term of surface area analysis. Observation of the surface area of modified SW-C500 adsorbents are shown in Table 4.7.

Table 4.7 Surface area of SW-C500 modified with 1, 3, 4, 5 and 6 M of H_3PO_4, H_2SO_4 and $ZnCl_2$

Adsorbents	Surface area (m^2/g) *
SW-C500	52.10 - 59.40
SW-C500-P1	14.03 ± 2.82
SW-C500-P3	5.72 ± 0.57
SW-C500-P4	3.18 ± 0.57
SW-C500-P5	2.25 ± 0.52
SW-C500-P6	1.49 ± 0.17
SW-C500-S1	19.17 ± 1.04
SW-C500-S3	5.53 ± 0.82
SW-C500-S4	3.82 ± 0.88
SW-C500-S5	2.50 ± 0.45
SW-C500-S6	2.11 ± 0.90
SW-C500-Z1	6.32 ± 0.76
SW-C500-Z3	4.09 ± 0.96
SW-C500-Z4	2.77 ± 0.40
SW-C500-Z5	2.61 ± 0.32
SW-C500-Z6	2.04 ± 0.57

*Mean ± S.D. (n=3)

Surface area of SW-C500 before modification was in range of 52.10 - 59.40 m^2/g and decreased after modification process. The surface area of obtained adsorbents obviously decreased as the concentration of modifying agent increased from 1 M to 3 M and slightly decreased in increasing the modifying agent concentration from 3 M to 6 M.

SEM analysis

This technique was used to exhibit the surface topography of modified and non-modified SW-C500. The adsorbents SW-C500-P3, SW-C500-S3 and SW-C500-Z3 were chosen to investigate the surface morphology compared to SW-C500 because the modification of surface with 3 M solution seems to nearly reach the optimal modification extent on surface. The SEM images are illustrated in Figure 4.6.
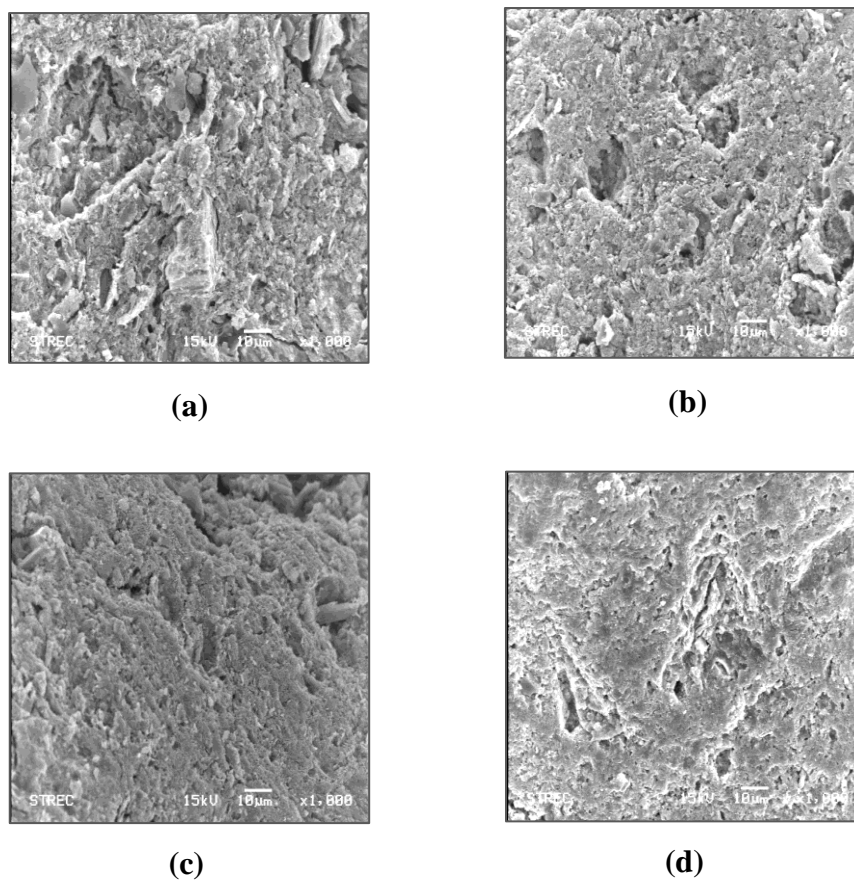

(a)   **(b)**

(c)   **(d)**

Figure 4.6 SEM images of (a) SW-C500, (b) SW-C500-P3, (c) SW-C500-S3 and (d) SW-C500-Z3 at 1000 magnifications.

Considering the appearance of the non-modified and modified material, the outer surface of the modified material was much smoother than the non-modified surface. The reduction of surface roughness of adsorbents obtained after modification may result in the reduction in adsorbent surface area as observed previously by area analysis.

Proximate elemental composition on surface was analyzed by SEM-EDX and shown in Table 4.8. The non-modified material predominantly contained carbon, oxygen, aluminium and silicon at approximately 42.1%, 36.8%, 3.5% and 7.9% respectively. The elemental composition on surface of the modified material changed after modification.

Table 4.8 The elemental compositions on SW-C500 adsorbents surface

Adsorbent	C (%)	O (%)	P (%)	S (%)	Zn (%)[a]	Cl (%)[a]
SW-C500	42.10	36.81	-	-	-	-
SW-C500-P3	23.40	51.80	3.84	-	-	-
SW-C500-S3	17.41	52.60	-	2.78	-	-
SW-C500-Z3	20.86	44.30	-	-	1.48	3.17

[a] atomic composition on surface

Considering the results shown in Table 4.8, the elemental carbon on surface of modified SW-C500 decreased according to the surface modification, acid content and $ZnCl_2$ salt probably covered the carbon surface resulting in a lower signal of carbon on surface. In case of surface modification with H_3PO_4, an increase in oxygen content and the presence of phosphorous indicate the presence of phosphate groups on surface after modification. For SW-C500-S3 material, the elemental oxygen and sulfur observed were from sulfate groups remaining on surface after modification.

In case of $ZnCl_2$, the atomic composition of Zn and Cl were observed. The composition of Zn:Cl ratios was found to be 1.48:3.17 %, it was clearly identified that the ratio of Zn:Cl on surface was closed to 1:2 of $ZnCl_2$. The result revealed that $ZnCl_2$ was accreted on to the adsorbent material in the form of $ZnCl_2$ salt. All SEM/EDX results confirm that the surface of SW-C500 was successfully modified.

4.1.2.2 Comparison of adsorption efficiency

The adsorbents obtained from using various modifying agent concentrations were used in the adsorption of ammonia in gas sample. The initial ammonia concentration (C_0) was in the range of 18-20 mmol/L. Breakthrough curves were constructed (Figure 4.7-4.9) and column efficiencies are summarized in Table 4.9.

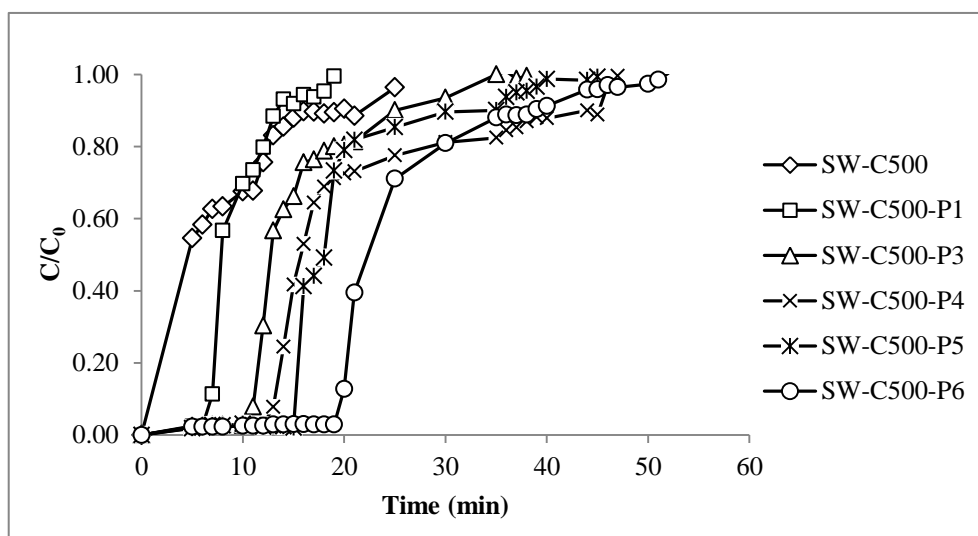**Figure 4.7** Breakthrough curve of ammonia adsorption by SW-C500 (C_0 19.45 mmol/L) and SW-C500 modified with 1, 3, 4, 5 and 6 M of H_3PO_4 (C_0 20.27, 19.11, 18.20, 21.02 and 19.06 mmol/L); column filled with 3 g adsorbent and gas flow rate 30 mL/min.

Figure 4.8 Breakthrough curve of ammonia adsorption by SW-C500 (C_0 19.45 mmol/L) and SW-C500 modified with 1, 3, 4, 5 and 6 M of H_2SO_4 (C_0 20.93, 19.49, 18.67, 19.05 and 19.64 mmol/L); column filled with 3 g adsorbent and gas flow rate 30 mL/min.
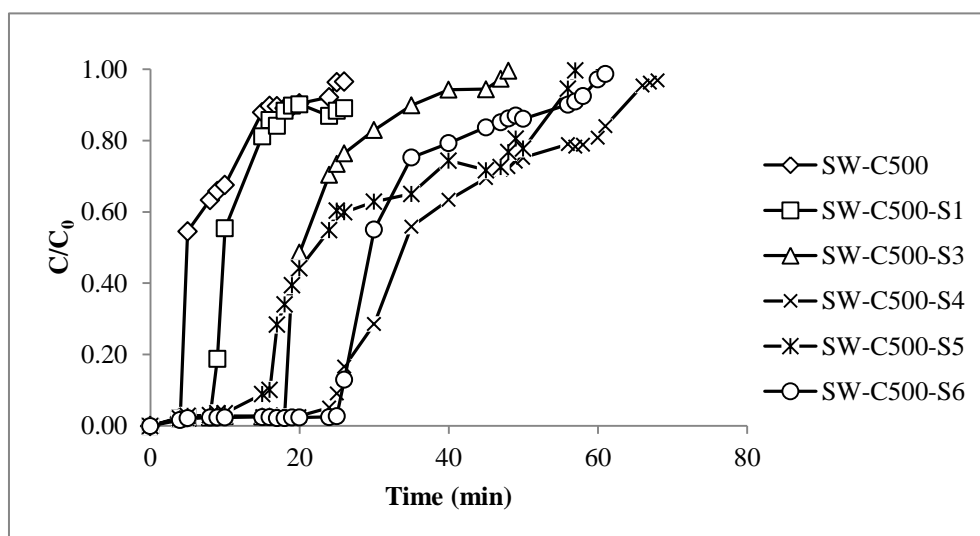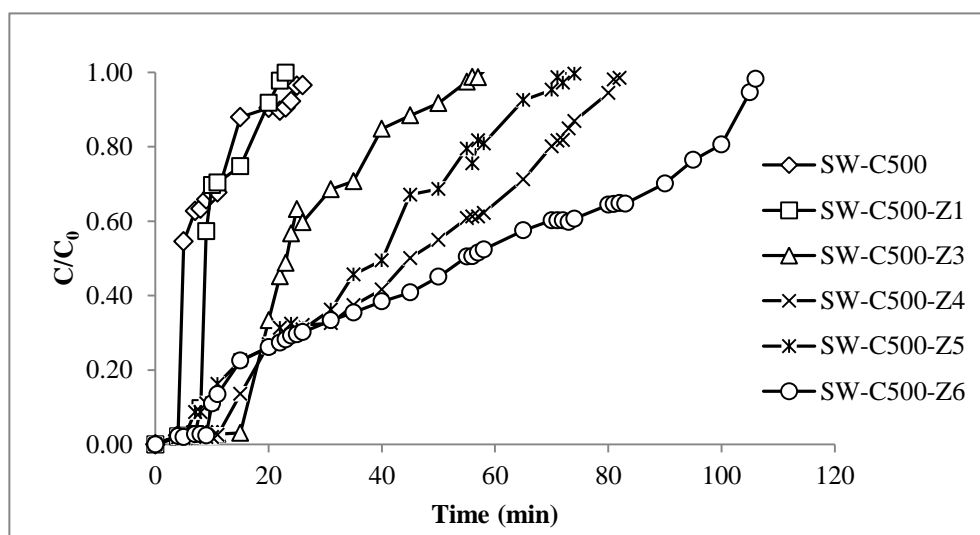

Figure 4.9 Breakthrough curve of ammonia adsorption by SW-C500 (C_0 19.45 mmol/L) and SW-C500 modified with 1, 3, 4, 5 and 6 M of $ZnCl_2$ (C_0 19.68, 19.66, 18.43, 20.08 and 18.26 mmol/L); column filled with 3 g adsorbent and gas flow rate 30 mL/min.

From breakthrough curves, column containing adsorbents prepared by using high modifying agent concentration (i.e. 3-6 M concentration) could retain ammonia in a long time before the column capacity was used up and the column efficiency was also high. Adsorbent materials modified with $ZnCl_2$ provided the best performance for ammonia adsorption followed by H_2SO_4 and H_3PO_4, respectively.

Table 4.9 Column efficiency in ammonia adsorption by SW-C500 modified with 1, 3, 4, 5 and 6 M of H_3PO_4, H_2SO_4 and $ZnCl_2$

Adsorbent	Column efficiency (mg/g) *
SW-C500	72.50 ± 2.88
SW-C500-P1	38.89 ± 2.81
SW-C500-P3	81.95 ± 0.79
SW-C500-P4	87.21 ± 3.32
SW-C500-P5	93.43 ± 5.98
SW-C500-P6	94.22 ± 1.04
SW-C500-S1	64.90 ± 0.16
SW-C500-S3	90.59 ± 2.87
SW-C500-S4	98.07 ± 6.56
SW-C500-S5	101.78 ± 3.26
SW-C500-S6	100.82 ± 1.15
SW-C500-Z1	48.26 ± 1.75
SW-C500-Z3	109.78 ± 5.60
SW-C500-Z4	118.28 ± 2.08
SW-C500-Z5	132.94 ± 2.42
SW-C500-Z6	148.77 ± 1.25

*Mean ± S.D. (n=3)

To better illustrate the effect of the modifying agent concentration on adsorbent adsorption efficiency, the column efficiency was plotted against the proton or Zn content found on adsorbent modified by using different modifying agent concentration (Figure 4.10).
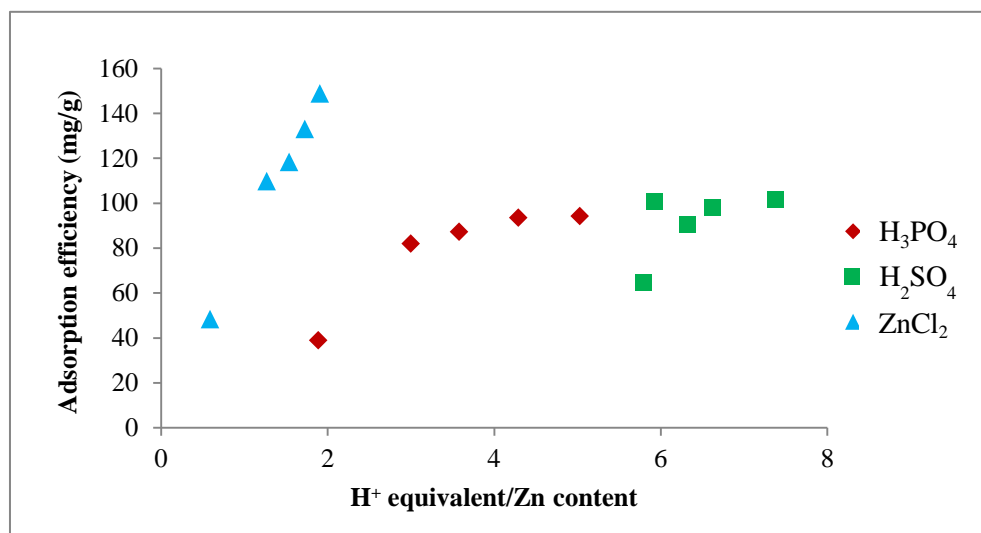

Figure 4.10 Adsorption efficiency profile in function of the H^+ or Zn content of SW-C500 modified with 1, 3, 4, 5 and 6 M of H_3PO_4, H_2SO_4 and $ZnCl_2$.

The results in Figure 4.10 show that ammonia adsorption efficiency is related to the amount of modifying agent on adsorbent surface. The higher amount of either H^+ or $ZnCl_2$ on adsorbent, the better the adsorbent could adsorb ammonia. The same increasing trend was observed in the case of the modification with H_3PO_4 and H_2SO_4. The adsorption efficiency increased rapidly with an increase in H^+ content from 2.85 to 3.96 mEq or from 6.75 to 7.28 mEq on adsorbents obtained from the modification with 1 and 3 M H_3PO_4 or H_2SO_4, respectively. An increase in acid concentration to 4-6 M in the modification did not result in a remarkable increase in H^+ content on adsorbents and consequently the adsorption efficiency. In case of $ZnCl_2$ modification, the adsorption efficiency increased continuously relating to the amount of Zn immobilized on adsorbent surface with the sharp increase in both Zn content and adsorption efficiency when increased $ZnCl_2$ concentration from 1 to 3 M in the modification.

To choose a suitable modifying agent for adsorbents preparation, it has to be compromised between the adsorption efficiency and the modification efficiency which concern the environmental satisfaction and cost of production. Hence, the relationship between adsorption efficiency and efficiency in modification of SW-C500 with 1, 3, 4, 5 and 6 M of H_3PO_4, H_2SO_4 and $ZnCl_2$ is illustrated in Figure 4.11-13. The results show that adsorption efficiency is notably increased with increasing the concentration of modifying agent from 1 to 3 M but slightly increased when used the concentration higher than 3 M. The highest modification efficiency observed in this experiment was obtained when modified the adsorbent with 1 M modifying agent and the modification efficiency declined afterward. Considering both the adsorption efficiency of the adsorbent obtained and the modification efficiency, H_3PO_4, H_2SO_4 and $ZnCl_2$ of 3 M concentration were chosen to prepare adsorbents.
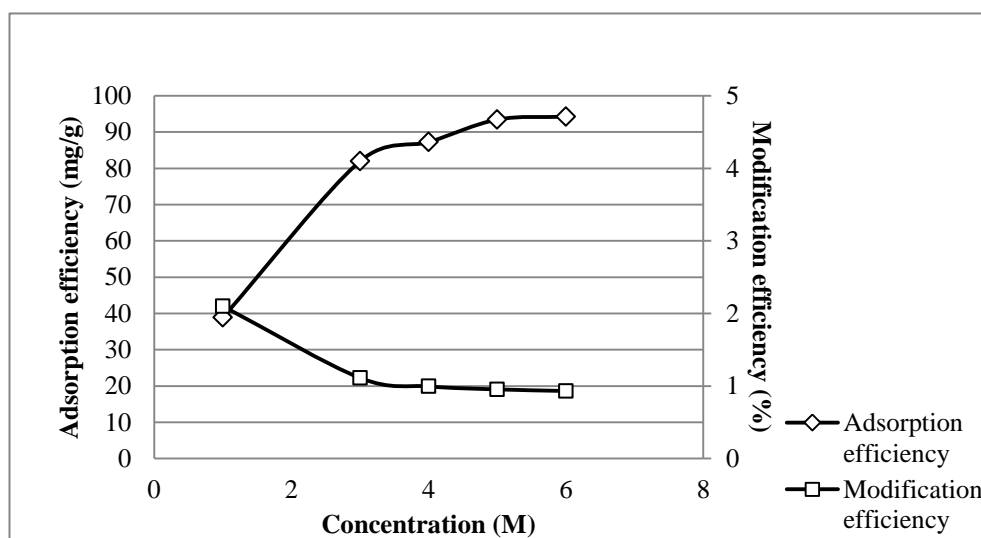

Figure 4.11 Adsorption efficiency and modification efficiency of SW-C500 modified with 1, 3, 4, 5 and 6 M of H_3PO_4.
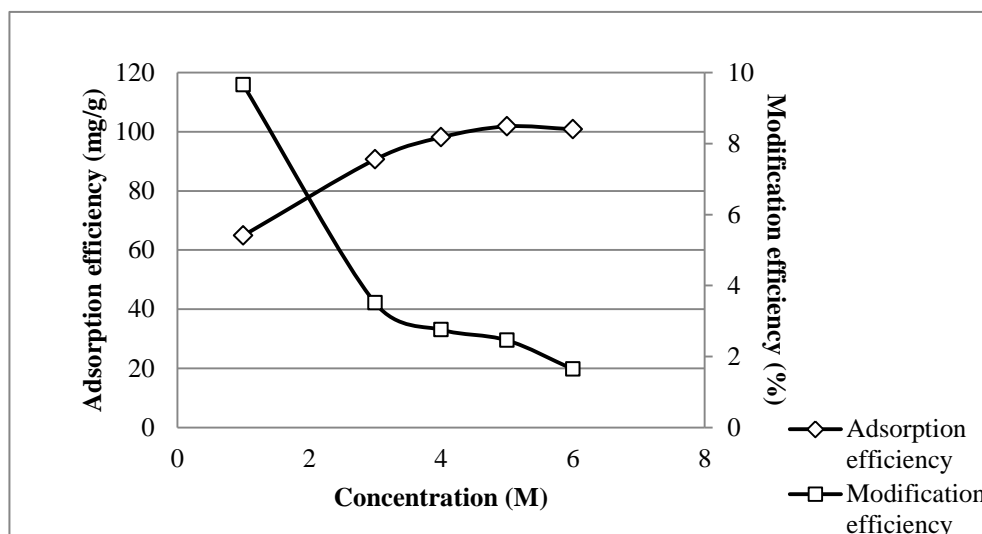
Figure 4.12 Adsorption efficiency and modification efficiency of SW-C500 modified with 1, 3, 4, 5 and 6 M of H_2SO_4.
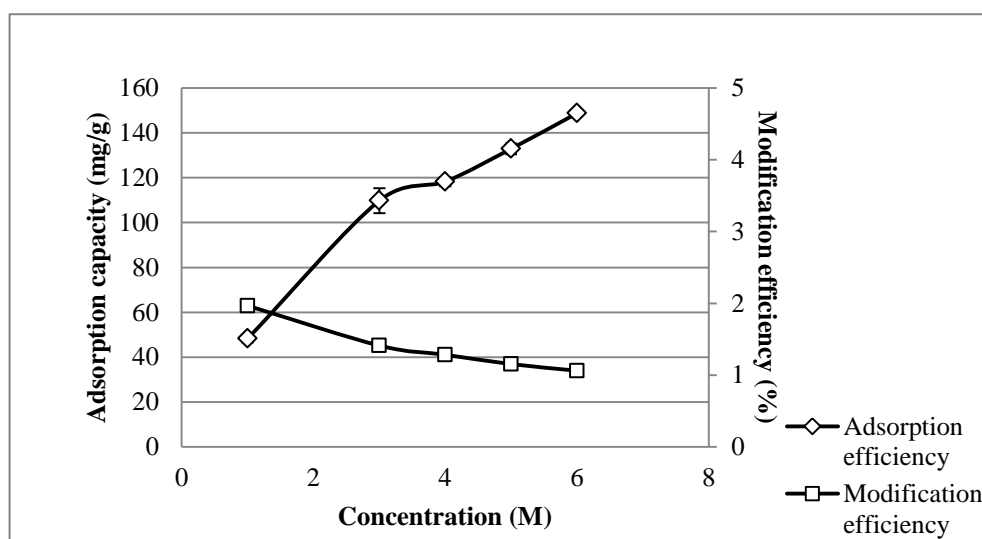

Figure 4.13 Adsorption efficiency and modification efficiency of SW-C500 modified with 1, 3, 4, 5 and 6 M of $ZnCl_2$.

4.2 Ammonia adsorption mechanism

To better comprehend the chemical adsorption of ammonia on surface, the reaction mechanism is necessary to elucidate. A proposed mechanism of ammonia adsorption on adsorbent material modified with H_3PO_4 and H_2SO_4 can be defined by Brønsted-Lowry acid-base reaction. Acid modified surface as Brønsted-Lowry acid is able to donate a proton (H^+) to ammonia, which is Brønsted-Lowry base. On the other hand, the mechanism of reaction between $ZnCl_2$ and NH_3 has not been well understood. In the area of carbon containing adsorbents preparation, $ZnCl_2$ are mostly used as activating agent to improve the porosity of adsorbent material [42]. There are a few data support in literature reporting the reaction of ammonia and $ZnCl_2$.

Petit *et al*. proposed the reaction of $ZnCl_2$ and NH_3 as shown in Scheme (1) [43]. Ammonium ions were generated by the reaction of ammonia with water and subsequently formed complex with zinc chloride as $ZnCl_2 \bullet NH_4Cl$ complex.
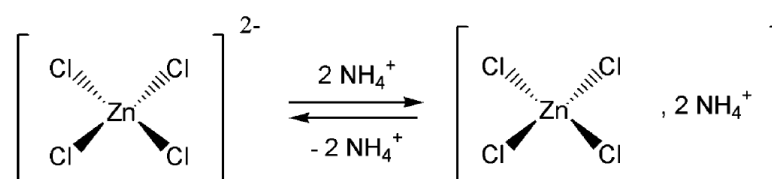
Scheme 4.2 The reaction of $ZnCl_2$ and ammonia [43]

Another aspect for the interaction of $ZnCl_2$ and NH_3 is proposed by Fortier *et al*.[44]. They have studied the reaction stoichiometry of $ZnCl_2$ and NH_3 under dry and humid conditions, they found that the dehumidified NH_3 gas will adsorb onto the $ZnCl_2$ impregnated activated carbon in higher extent than humidified NH_3 gas. It created a layer of product "$Zn(NH_3)_2Cl_2$" on the adsorbent surface, the reaction stoichiometric ratio of NH_3 to $ZnCl_2$ was found to be 1.56:1 and 1.65:1 under humid and dry condition, respectively. They defined that the extent of NH_3 and $ZnCl_2$ reaction depends on the partial pressure of ammonia over the adsorbent. In order to get the stoichiometric ratio of reaction of NH_3 to $ZnCl_2$ up to 2:1, they increased the pressure of the ammonia gas going through the adsorbent material under humid conditions. The reaction mechanism of $ZnCl_2$ and NH_3 is shown in equation (1).

$$2NH_3 \text{ (g)} + ZnCl_2 \text{ (ads)} \rightleftharpoons Zn(NH_3)_2Cl_2 \text{ (ads)} \qquad (1)$$
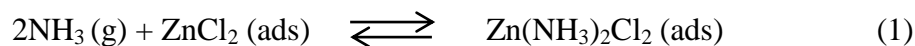
Fortier mentioned that the discrepancies between their research study and Petit's research study is that, Petit showed the formation of $ZnCl_2 \cdot NH_4Cl$, which is the compound that can strongly adsorb on adsorbent materials but they saw no evidence of $Zn(NH_3)_2Cl_2$, it is perhaps that the compounds were formed but easily desorbed upon a clean air purge.

Moreover, there is another research studies by Wilcox that showed the identical formation of $ZnCl_2$ and NH_3 as proposed by Fortier *et al*. but there was some argument against Fortier's research study. Wilcox revealed that the parent network of $ZnCl_2$ was completely destructed by ammonia adsorption to form $ZnCl_2(NH_3)_2$. The reformation of $ZnCl_2$ from $ZnCl_2(NH_3)_2$ did not occur unless the ammonia was driven off at about 220 °C and further heating to the melting point of $ZnCl_2$ at 317 °C would allow the recrystallization of $ZnCl_2$ to occur. The reaction of $ZnCl_2$ and NH_3 is shown in Figure 4.14 [45].
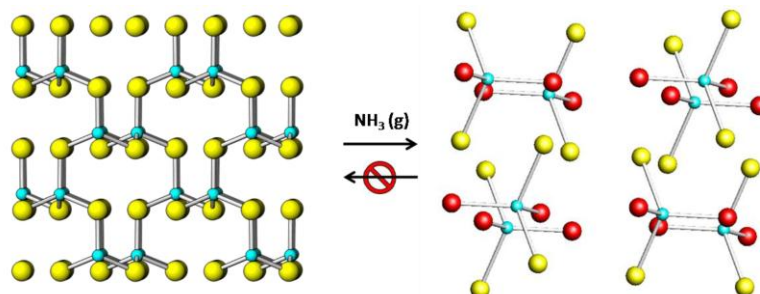
Figure 4.14 Structural change from the $ZnCl_2$ network (left) to the molecular structured $ZnCl_2(NH_3)_2$ (right) upon ammonia sorption demonstrating the sorptive destructive mechanism [45].

In summary, the possible adsorption mechanisms of ammonia over adsorbent modified with $ZnCl_2$ occur via the formation of $ZnCl_2(NH_3)_2$ under dry condition and $ZnCl_2(NH_3)_2$ and/or $ZnCl_2 \cdot NH_4Cl$ under humid condition. In our study, the presence of ammonia adducts on adsorbents was confirmed by FT-IR.

Confirmation of ammonia adsorption on adsorbent materials

Figure 4.15 and 4.16 show the FT-IR spectra of adsorbent materials modified with 3M H_3PO_4 and H_2SO_4 before and after ammonia adsorption. IR spectra of non-modified adsorbents were also illustrated and no significant difference was observed in the IR spectra of non-modified and modified adsorbents. It is likely that only small amount of modifying agent was retained on adsorbents surface and FT-IR technique was unable to detect the change on adsorbents surface. After NH_3 adsorption, a new absorption band around 3300-3000 cm^{-1} occurred, which may be attributed to the overtones of the O–H and N–H stretching vibrations that overlapped each other [12]. Another absorption band around 1400 cm^{-1} exhibited after NH_3 adsorption is close to the vibration frequency of NH_4^+ chemically adsorbed on Brønsted acid sites [12]. From FT-IR spectra, the results agreed well with the mechanism of Brønsted-Lowry acid-base reaction.

In case of $ZnCl_2$ (Figure 4.17), the FT-IR spectra show an appearance of the vibration band of NH_4^+ at 1400 cm^{-1}. Thus, in this study, the mechanism of ammonia adsorption on $ZnCl_2$ surface might occur via the formation of $ZnCl_2 \cdot NH_4Cl$, as proposed by Petit *et al.*
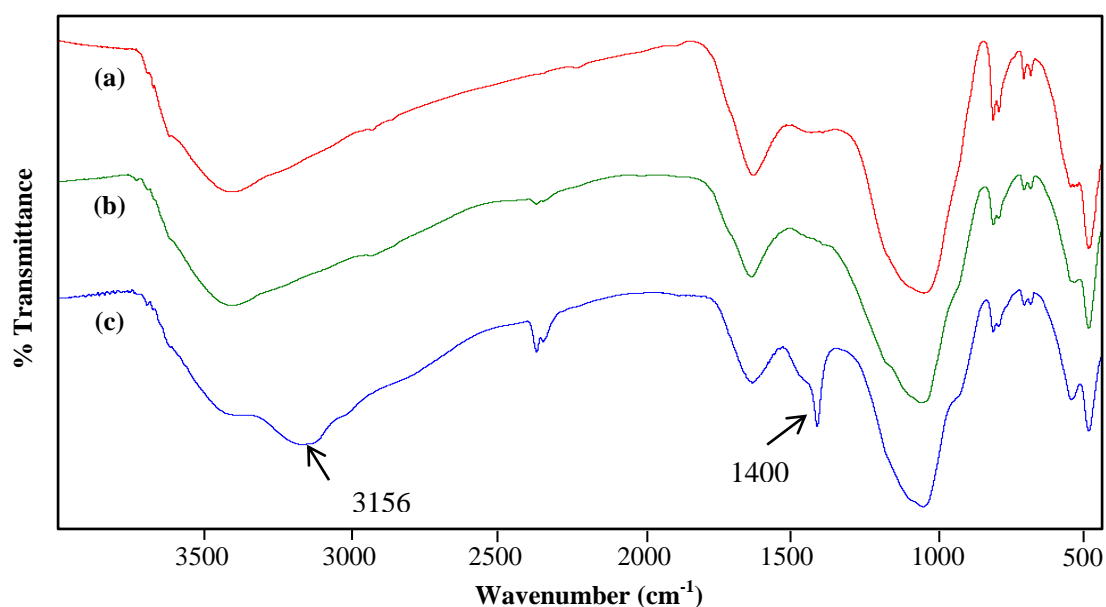

Figure 4.15 FT-IR spectra of (a) SW-C500, (b) SW-C500-P3 and (c) SW-C500-P3 after adsorbing NH_3.
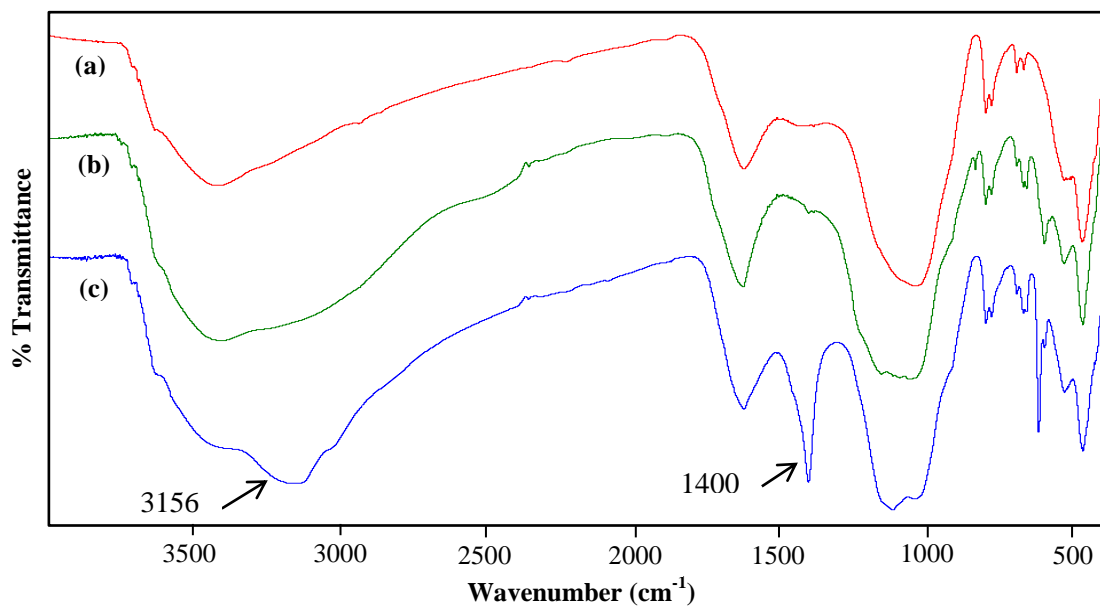
Figure 4.16 FT-IR spectra of (a) SW-C500, (b) SW-C500-S3 and (c) SW-C500-S3 after adsorbing NH_3.
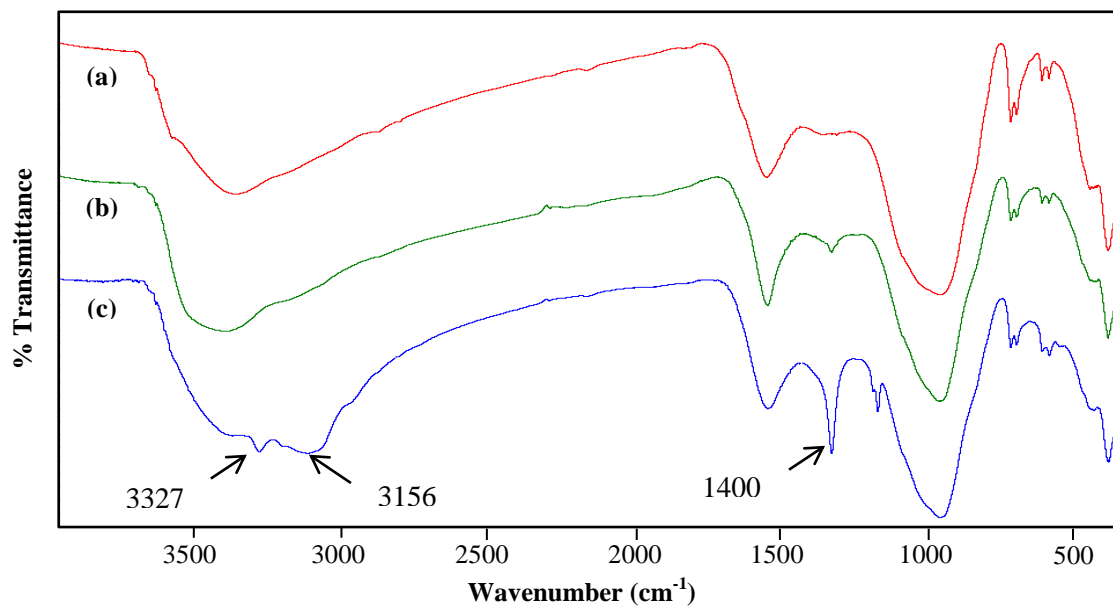

Figure 4.17 FT-IR spectra of (a) SW-C500, (b) SW-C500-Z3 and (c) SW-C500-Z3 after adsorbing NH_3.

4.3 Study of the effect of adsorption parameter

4.3.1 Effect of initial ammonia concentration

To study the effect of ammonia concentration on the adsorption efficiency of adsorbent materials (SW-C500-P3, SW-C500-S3 and SW-C500-Z3), N_2 flow rate was adjusted to be 50 and 70 mL/min whereas the ammonia flow rate was fixed at 5 mL/min. Breakthrough curve and column adsorption efficiency was observed (Figure 4.18, 4.19, Table 4.10). When the N_2 flow rate was increased from 50 to 70 mL/min, ammonia concentration in the sample gas decreased from 18.20-21.02 mmol/L to 14.38-15.42 mmol/L, as a result, the column could retain ammonia gas for longer time before breakthrough occurred (i.e. the retention time increased from 5-18 min to 6-27 min).

Considering the adsorption efficiency under different ammonia concentration, the adsorption efficiency of adsorbent slightly increased when ammonia concentration in gas mixture increased as shown in Table 4.10. The increase in concentration would increase the mass transfer of ammonia from the gas phase to the solid phase, resulting in a higher amount of ammonia adsorbed on adsorbent.

Table 4.10 Effect of ammonia concentration on column efficiency

N_2 flow rate (mL/min)	[NH_3] (mmol/L)	Column efficiency (mg/g)*		
		SW-C500-P3	**SW-C500-S3**	**SW-C500-Z3**
50	18.20-21.02	81.95 ± 0.79	90.59 ± 2.87	109.78 ± 5.60
70	14.38-15.42	79.45 ± 2.93	81.97 ± 1.55	96 ± 1.26

*Mean ± S.D. (n=3)

Figure 4.18 Breakthrough curve of ammonia adsorption by SW-C500 (C_0 19.45 mmol/L), SW-C500-P3 (C_0 19.11 mmol/L), SW-C500-S3 (C_0 19.49 mmol/L) and SW-C500-Z3 (C_0 19.66 mmol/L) at initial N_2 flow rate of 50 mL/min; adsorbent 3 g and gas flow rate 30 mL/min.

Figure 4.19 Breakthrough curve of ammonia adsorption by SW-C500 (C_0 15.42 mmol/L), SW-C500-P3 (C_0 14.87 mmol/L), SW-C500-S3 (C_0 14.38 mmol/L) and SW-C500-Z3 (C_0 14. 83 mmol/L) at initial N_2 flow rate of 70 mL/min; adsorbent 3 g and gas flow rate 30 mL/min.

4.3.2 Effect of column size on adsorption capacity

In order to evaluate the performance in ammonia adsorption in a larger scale, a larger column was employed. A homemade glass column with 20 cm length and 1.0 cm id. was used in this experiment. The column was packed with 9 g of adsorbents, which is three folds higher than adsorbent mass used in the column with 5 cm length and 1.0 cm id. NH_3 and N_2 flow rate were fixed at 5 and 50 mL/min, respectively. Breakthrough curve of ammonia adsorption by the new column is shown in Figure 4.20.
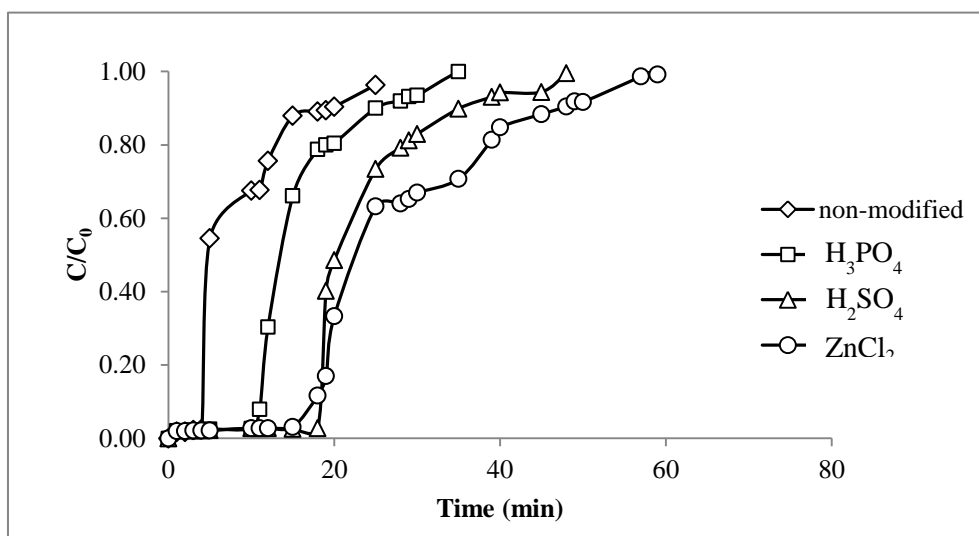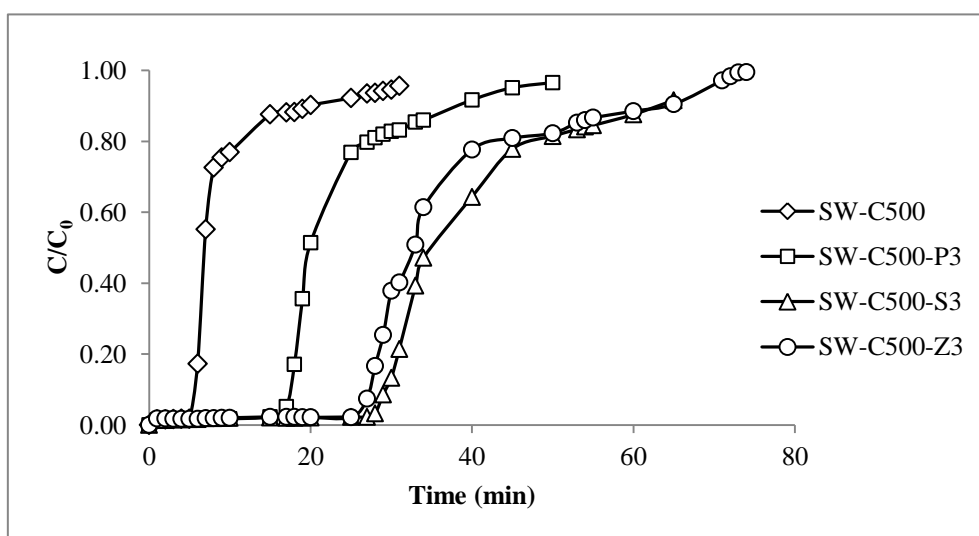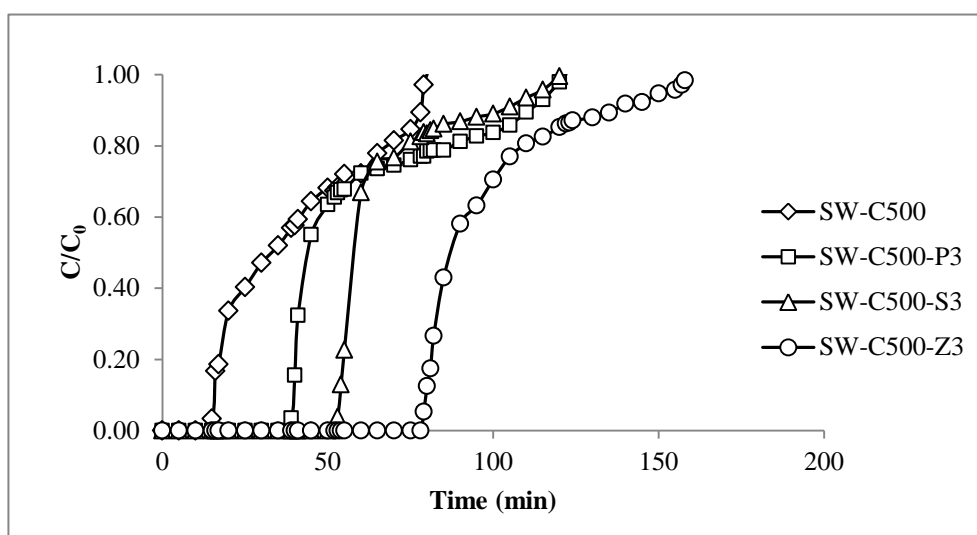

Figure 4.20 Breakthrough curve of ammonia adsorption by SW-C500 (C_0 19.09 mmol/L) SW-C500-P3 (C_0 20.65 mmol/L), SW-C500-S3 (C_0 20.75 mmol/L) and SW-C500-Z3 (C_0 20.73 mmol/L); adsorbent 9 g and gas flow rate 30 mL/min.

For the new column applied, the results revealed that the column could retain ammonia gas for 10-75 min. before ammonia breakthrough occurred, which was about 2-3 folds longer than breakthrough time of the small column (5-18 min.). This result correlates with the increase in adsorbents mass that was also increased 3 folds. Interestingly, the accumulated amount of ammonia adsorbed in the large column was lower than that observed in the small column. The column efficiency of large column packed with SW-C500-P3, SW-C500-S3 and SW-C500-Z3 are 46.48±1.87,

61.04±1.68 and 69.10±4.78 mg/g, respectively (See Table 4.9 for the column efficiency of a small column). It is probably because the diffusion of gas through adsorbent bed occurs in different manner when it flows through column of different size. Hence, the column size or diameter is one of the parameters that strongly affect the efficiency in ammonia gas adsorption.

CHAPTER V

CONCLUSION

5.1   Conclusion

A low cost sewage sludge-based adsorbent for ammonia gas removal was successfully prepared. The adsorbent was prepared by carbonization of exhausted sewage sludge and modification with H_3PO_4, H_2SO_4 or $ZnCl_2$. The physical properties of obtained adsorbents were characterized by surface area analysis (BET method), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA) meanwhile the chemical properties were characterized by titration method, flame atomic absorption spectroscopy (FAAS) and Fourier transforms infrared spectroscopy (FT-IR). Ammonia adsorption study was carried out in a fixed bed reactor. The ammonia adsorption efficiency and breakthrough curve was obtained from adsorption study.

Regarding the effect of carbonization temperature, the results showed that sewage sludge undergone the carbonization at 500 °C (SW-C500) had higher efficiency in ammonia adsorption than the non-carbonized (SW-NC) and sewage sludge carbonized at 300 °C (SW-C300). The subsequent study was to modify SW-C500 with 1, 3, 4, 5 and 6 M of H_3PO_4, H_2SO_4 or $ZnCl_2$. In raising the modifying agent concentration from 1 to 3 M, efficiency in modification and surface area of adsorbent surface decreased progressively, while the adsorption efficiency of the obtained adsorbents increased. The modifying agents at 3 M concentration were chosen as a compromise between modification efficiency and adsorbent adsorption efficiency. Hence, the suitable condition for adsorbent preparation was the carbonization at 500 °C and modification with 3M of H_3PO_4, H_2SO_4 and $ZnCl_2$, the ammonia adsorption efficiency of the adsorbents (SW-C300-P3, SW-C300-S3, SW-C300-Z3) was found to be 81.95, 90.59, 109.78 mg/g, respectively.

The effect of initial ammonia concentration on the adsorption efficiency of SW-C300-P3, SW-C300-S3, and SW-C300-Z3 was further investigated. When the ammonia concentration in the gas sample was decreased from 18.20-21.02 mmol/L to 14.38-15.42 mmol/L, the columns could retain ammonia for longer time before breakthrough occurred. The retention time increased from 5-18 min to 6-27 min.

The performance in ammonia adsorption in a larger scale was also evaluated by using a column of larger size and higher amount of adsorbents. The results revealed that the column could retain ammonia gas for 10-75 min. before ammonia breakthrough occurred, which was about 2-3 folds longer than breakthrough time of the small column (5-18 min.)

The ammonia adsorption mechanism on adsorbent material modified with H_3PO_4 and H_2SO_4 can be defined by Brønsted-Lowry acid-base reaction. Meanwhile, the reaction of $ZnCl_2$ and NH_3 probably occurs via the formation of $ZnCl_2 \cdot NH_4Cl$ on surface.

5.2   Suggestion of future work

- The present method should be applied to the adsorption in real sample treatment activity such as, in the agricultural activities or farm.
- This research needs further study of the regeneration of adsorbent material after exposed to ammonia gas.

REFERENCES

[1]   Chung, Y. C.; Lin, Y. Y.; Tseng, C. P. Removal of high concentration of NH3 and coexistent H2S by biological activated carbon (BAC) biotrickling filter. Bioresource Technology. 96 (2005) 1812–1820.

[2]   Ogejo, J. A.; Senger, R. S.; Zhang, R. H. Global sensitivity analysis of a process-based model for ammonia emissions from manure storage and treatment structures. Atmospheric Environment. 44 (2010) 3621-3629.

[3]   Dianwu, Z.; Anpu, W. Estimation of anthropogenic ammonia emissions in Asia. Atmospheric Environment. 28 (1994) 689-694.

[4]   Jawjit, W.; Kroeze, C.; Rattanapan, S. Greenhouse gas emissions from rubber industry in Thailand. Journal of Cleaner Production. 18 (2010) 403-411.

[5]   Bandosz, T. J. and Petit, C. On the reactive adsorption of ammonia on activated carbons modified by impregnation with inorganic compounds. Journal of Colloid and Interface Science. 338 (2009) 329-345.

[6]   Pagans, E. L.; Font, X.; S´anchez, A. Biofiltration for ammonia removal from composting exhaust gases. Chemical Engineering Journal. 113 (2005) 105-110.

[7]   Couvert, A.; Sanchez, C.; Laplanche, L.; Renner, C. Scrubbing intensification for sulphur and ammonia compounds removal. Chemosphere. 70 (2008) 1510-1517.

[8]   Jia, G.; Wang, S. X.; Yan, L. C.; Aik, C. L. Adsorption of NH_3 onto activated carbon prepared from palmshells impregnated with H_2SO_4. Journal of Colloid and Interface Science. 281 (2005) 285-290.

[9]   Smith, K. M.; Fowler , G.D.; Pullket, S.; Graham, N.J.D. Sewage sludge-based adsorbents: A review of their production, properties and use in water treatment applications. Water Research. 43 (2009) 2569-2594.

[10]   Kemmer, F. N.; Robertson, S.R.; Mattix, R.D. Sewage treatment process. Nalco Chemical Company. US Patent Office. 1971, Patent No. 3,619,420.

[11]   Seredych, M.; Strydom, C.; Bandosz, T. J. Effect of fly ash addition on the removal of hydrogen sulfide from biogas and air on sewage sludge-based composite adsorbents. Waste Management. 28 (2008) 1983-1992.

[12]   Huang, C. C.; Li, H. S.; Chen, C. H. Effect of surface acidic oxides of
       activated carbon on adsorption of ammonia. Journal of Hazardous Materials.
       159 (2008) 523-527.

[13]   U.S. Department of health and human services. Occupational safety and health
       guideline for ammonia. The United State of America: Standard development
       and technology transfer. National institute for occupational safety and
       health, 1992.

[14]   WBK & Associates Inc. Assessment report on ammonia for developing
       ambient air quality objectives volume I. Canada: Alberta Environment,
       Science and Standards Branch, January 2004.

[15]   Anderson, N.; Strader, R.; Davidson, C. Airborne reduced nitrogen: ammonia
       emissions from agriculture and other sources. Environment International. 29
       (2003) 277- 286.

[16]   Zhao, D.; Wang, A. Estimation of anthropogenic ammonia emissions in Asia.
       Atmospheric Environment., 28 (1994) 689-694.

[17]   Sutton, M. A.; Dragosits, U.; Tang, Y.S.; Fowler, D. Ammonia emissions
       from non-agricultural sources in the UK. Atmospheric Environment. 34
       (2000) 855-869.

[18]   Ramirez-Lopez, E. M.; Corona-Hernandez, J.; Avelar-Gonzalez, F. J.; Omil,
       F.; Thalasso, F. Biofiltration of methanol in an organic biofilter using peanut
       shells as medium. Bioresource Technology. 101 (2010) 87-91.

[19]   The Clean Air Technology Center (CATC). Using bioreactors to control air
       pollution. The United State of America: U.S. Environmental Protection
       Agency, September 2003.

[20]   Busca, G.; Pistarino C. Abatement of ammonia and amines from waste gases:
       a summary. Journal of Loss Prevention in the Process Industries. 16 (2003)
       157-163.

[21]   Govind, R. Biofiltration: an innovative technology for the future. Department
       of Chemical Engineering, University of Cincinnati.

[22]   Liang, Y.; Quan, X.; Chen, J.; Chung, J. S.; Sung, J. Y.; Chen, S.; Xue, D.; Zhao, Y. Long-term results of ammonia removal and transformation by biofiltration. Journal of Hazardous Materials. B80 (2000) 259-269.

[23]   Rouquerol, F.; Rouquerol, J.; Sing, K. Adsorption by powders and porous solids principles, methodology and applications, MPG Books Ltd, England, 1999.

[24]   Seredych, M.; Bandosz, T. J. Desulfurization of Digester Gas on Catalytic carbonaceous Adsorbents: Complexity of Interactions between the Surface and Components of the Gaseous Mixture. Industrial & Engineering Chemistry Research. 45 (2006) 3658-3665.

[25]   Carmody, O.; Frost, R.; Xi, Y.; K, S. Surface characterisation of selected sorbent materials for common hydrocarbon fuels. Surface Science. 601 (2007) 2066-2076.

[26]   Andreiadis, E. S. Breakthrough curves: Determination of specific parameters. Chemical Engineering Department. Polytechnic University of Bucharest.

[27]   Park, M.; Knaebel, K. S. Adsorption Breakthrough Behavior: Unusual Effects and Possible Causes. AIChE Journal. 38 (1992) 660-670.

[28]   Petit, C.; Bandosz, T. J. Complexity of ammonia interactions on activated carbons modified with V_2O_5. Journal of Colloid and Interface Science. 325 (2008) 301-308.

[29]   Kanaebel, K. S. Adsorbent selection. Adsorption research Inc. Duplin, OH, 1-23.

[30]   Thomas, W. J.; Crittenden, B. Adsorption Technology and Design. The Spartan Press Ltd, Great Britain. 1998.

[31]   Rozada, F.; Otero, M.; Moran, A. Garcia, A.I. Activated carbons from sewage sludge and discarded tyres: Production and optimization. Journal of Hazardous Materials. B124 (2005) 181-191.

[32]   Torregrosa-Mac, R.; Martin-Martinez, J. M.; Mittelmeijer-Hazeleger, M. C. Porous texture of activated carbons modified with carbohydrates. Carbon. 35 (1997) 447-453.

[33] Ju, S.; Chun-hu, L.; Mao-qian, M.; Zhi, Y. Surface characterization and SO_2 removal activity of activated semi-coke with heat treatment. New carbon materials. 23(1) (2008) 37-43.

[34] Bashkova, S.; Bagreev, A.; Bandosz, T. J. Adsorption/Oxidation of CH3SH on Activated Carbons Containing Nitrogen. Langmuir. 19 (2003) 6115-6121.

[35] Chzang, P. C.; You, J. H. Use of Sewage Sludge for Manufacturing Adsorbents. The Canadian Journal of Chemical Engineering. 65 (1987) 922-927.

[36] Wen, Q.; Li, C.; Cai, Z.; Zhang, W.; Gao, H.; Chen, L.; Zeng, G.; Shu, X.; Zhao, Y. Study on activated carbon derived from sewage sludge for adsorption of gaseous formaldehyde. Bioresource Technology. 102 (2011) 942-947.

[37] Bagreev, A.; Bandosz, T. J. H_2S Adsorption/oxidation on materials obtained using sulfuric acid activation of sewage sludge-derived fertilizer. Journal of Colloid and Interface Science. 252 (2002) 188-194.

[38] Sharanov, V. E.; Aristov, Y. I. Ammonia adsorption by $MgCl_2$, $CaCl_2$ and $BaCl_2$ confined to porous alumina: the fixed bed adsorber. Reaction Kinetics and Catalysis letters. 85 (2005) 183–188.

[39] Le Leuch, L. M.; Bandosz, T. J. The role of water and surface acidity on the reactive adsorption of ammonia on modified activated carbons. Carbon. 45 (2007) 568–578.

[40] Petit, C.; Bandosz, T. J. Role of surface heterogeneity in the removal of ammonia from air on micro/mesoporous activated carbons modified with molybdenum and tungsten oxides. Microporous and Mesoporous Materials. 118 (2009) 61–67.

[41] Rodrigues, C. C.; de Moraes Jr, D.; da Nobrega, S. W.; Barboza, M. G. Ammonia adsorption in a fixed bed of activated carbon. Bioresource Technology. 98 (2007) 886-891.

[42] Gomez, J. G.; Garcia, A. M.; Diez, M. A.; Garcia, C. G.; Ray, E. S. Preparation and characterization of activated carbons from impregnation pitch by $ZnCl_2$. Applied Surface Science. 252 (2006) 5976-5979.

[43] Petit, C.; Karwacki, C.; Peterson, G.; Bandosz, T. J. Interactions of ammonia with the surface of microporous carbon impregnated with transition metal chlorides. <u>Journal of Physical Chemistry C</u>. 111 (2007) 12705-12714.

[44] Fortier, H.; Westreich, P.; Selig, S.; Zelenietz, C. Dahn, J. R. Ammonia, cyclohexane, nitrogen and water adsorption capacities of an activated carbon impregnated with increasing amounts of $ZnCl_2$, and designed to chemisorb gaseous NH_3 from an air stream. <u>Journal of Colloid and Interface Science</u>. 320 (2008) 423-435.

[45] Wilcox, R. J. Sorption to Dissolution: The Reactivity of Small Molecules with Condensed Phase Metal Halide Networks. A dissertation or thesis submitted to the Graduate Faculty of North Carolina State University. Department of Chemistry, North Carolina State University. Raleigh, North Carolina, 2009.

VITA

Miss Kanchalar Keeratirawee was born on April 3, 1980 in Sisaket, Thailand. She received her Bachelor degree of Science from Burapha University in 2003. After that, she has been a graduated student at the Department of Chemistry Chulalongkorn University and become a member of Environmental Analysis Research Unit under supervision of Assistant Professor Dr. Fuangfa Unob. She finished her Master's degree of Science in 2012. The present address is 92/5 Moo 5, Rat-utid Road, Kanthararom, Sisaket, Thailand, 33130. Contact number is 084-285-4285.