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**REMOVAL OF HUMIC ACIDS FROM SYNTHETIC WASTEWATER
BY RICE HUSK ASH AND MODIFIED RICE HUSK ASH**



Mr. Eakachai Prapalimrunsi

**A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Environmental Science**

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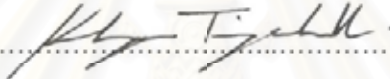
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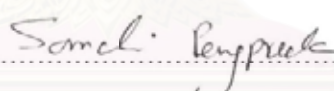
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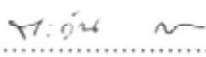
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งานวิจัยนี้ได้พัฒนาการใช้เถ้าแกลบซึ่งเป็นวัสดุเหลือทิ้งจากการเกษตรมาเป็นวัสดุดูดซับที่มีราคาถูกสำหรับการลดปริมาณกรดฮิวมิกในน้ำ จากผลการทดลองเบื้องต้นแสดงให้เห็นถึงความเป็นไปได้ในการใช้เถ้าแกลบมาเป็นวัสดุดูดซับดูดซับกรดฮิวมิกในน้ำ โดยทำการเตรียมเถ้าแกลบที่ผ่านการปรับสภาพด้วยสารละลาย HCl ก่อนนำไปเผาที่อุณหภูมิ 700 องศาเซลเซียส หารลักษณะเฉพาะทางกายภาพและทางเคมีของเถ้าแกลบที่เตรียมได้ และศึกษาสมบัติการดูดซับกรดฮิวมิกด้วยวิธีแบบแบทช์ โดยมีตัวแปรได้แก่ ระยะเวลาในการดูดซับ พีเอช และความเข้มข้นเริ่มต้นของสารละลายกรดฮิวมิก พบว่าภาวะที่เหมาะสมในการลดปริมาณกรดฮิวมิก คือ ใช้ระยะเวลาในการดูดซับนาน 60 นาที และที่พีเอชเท่ากับ 3.0 สามารถลดปริมาณกรดฮิวมิกได้สูงสุด แสดงให้เห็นว่าเถ้าแกลบที่เตรียมได้สามารถใช้ในการบำบัดน้ำ พฏิกิริมการดูดซับที่เกิดขึ้นเป็นไปตามแบบจำลองการดูดซับของแลงเมียร์และฟรุนด์ลิชโดยมีความสามารถในการดูดซับสูงสุดเท่ากับ 2.7 มิลลิกรัมต่อกรัมที่พีเอชเท่ากับ 6.0 นอกจากนี้ยังได้ทำการดัดแปรพื้นผิวของเถ้าแกลบด้วย 3-aminopropyltriethoxysilane และศึกษาสมบัติการดูดซับกรดฮิวมิกในน้ำตามวิธีข้างต้น พบว่าเถ้าแกลบที่ทำการดัดแปรพื้นผิวให้ประสิทธิภาพในการลดปริมาณกรดฮิวมิกที่ดีกว่าเถ้าแกลบ โดยภาวะที่เหมาะสมในการดูดซับคือ ใช้เวลาในการดูดซับนาน 30 นาที ที่ช่วงพีเอช 3.0-4.0 พฏิกิริมการดูดซับที่เกิดขึ้นเป็นไปตามแบบจำลองการดูดซับของแลงเมียร์โดยมีความสามารถในการดูดซับสูงสุดเท่ากับ 8.2 มิลลิกรัมต่อกรัมที่พีเอชเท่ากับ 6.0 และทำการศึกษาการดูดซับกรดฮิวมิกในน้ำแบบคอลัมน์พบว่าวัสดุดูดซับที่เตรียมได้สามารถใช้ในการบำบัดน้ำทั้งวิธีแบบแบทช์และคอลัมน์ นอกจากนี้ยังทำการเปรียบเทียบประสิทธิภาพในการดูดซับกรดฮิวมิกในน้ำกับถ่านกัมมันต์ทางการค้าซึ่งพบว่ามีประสิทธิภาพที่ไม่แตกต่างกันอย่างมีนัยสำคัญ และพบว่าวัสดุดูดซับที่เตรียมได้สามารถใช้ดูดซับกรดฮิวมิกในน้ำผิวดินได้

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An attempt on the use of rice husk ash (RHA), an agricultural waste, as an adsorbent for the adsorption of humic acids from water was studied. Preliminary studies have been shown the feasibility of rice husk ash for humic acids removal from water. The adsorbents were characterized for its various physico-chemical properties. Batch studies were performed to evaluate the influences of various experimental parameters such as contact time, pH and initial concentration on the adsorption of humic acids. Optimum conditions for humic acids adsorption were found as follows, 60 min equilibrium time and initial pH 3.0. Equilibrium data obtained have been found to agree with both Langmuir and Freundlich equations. The maximum adsorption capacity of rice husk ash was 2.7 mg/g, at pH 6.0. In addition, rice husk ash was modified with 3-aminopropyltriethoxysilane. Again, the adsorption behavior of the modified rice husk ash (RHA-NH₂) was studied. Optimum conditions for humic acids adsorption were found to be 30 min equilibrium time and initial pH in the range of 3.0-4.0. The results showed that the adsorption capacity of the modified rice husk ash was higher than that of rice husk ash. Experimental data fitted well into the Langmuir equation and the maximum adsorption capacity was 8.2 mg/g, at pH 6.0. The column method was also performed. It was found that the prepared rice husk ash can be used in both batch and column methods for water treatment. The comparative efficiency of rice husk ash and commercial activated carbon to adsorb humic acids from water was studied. The result showed that adsorption efficiency of the new rice husk ash adsorbents was not significantly different from commercial activated carbon. The adsorbents were applied for humic acids removal from surface water.

Inter-Department...Environmental Science... Student's signature. Eakachai Prapalimrungsri.
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LIST OF SYMBOLS AND ABBREVIATIONS

°C	Degree Celsius
µg	Microgram
cm	Centimeter
DBP	Disinfection by-product
g	Gram
h	Hour
HA	Humic acids
L	Liter
M	Mortality
min	Minute
mL	Milliliter
nm	Nanometer
ppb	Parts per billion
ppm	Parts per million
RHA	Rice husk ash
RHA-NH ₂	Modified rice husk ash
SD	Standard deviation
THM	Trihalomethane
EPA	Environmental Protection Agency
UV-vis	Ultra violet-visible
WHO	World Health Organization

CHAPTER I

INTRODUCTION

1.1 Statement of the problem

Humic acids (HA) are one of the major components of humic substances which arise by the microbial degradation of biomolecules. The presence of humic substances in water introduces a yellowish to brown color. Moreover, high affinity of humic substances for complexation with various pollutants including heavy metals and pesticides causes contamination of ground and surface water. In addition, HA will form very toxic disinfection by-products; i.e. chlorinated organic compounds for example trihalomethanes (THMs), which exhibit mutagenic properties during chlorination step in drinking water treatment [1, 2] and have their presence limited to 100 ppb in potable water by the World Health Organization. Thus, removal of HA from surface water or wastewater is very important.

Adsorption is one of the efficient methods in HA removal. In the past years, several adsorbents have been employed for HA adsorption including activated carbon [3, 4], clays [5], zeolite [6], chitosan [7] and metal-modified silica [8]. However, those adsorbents and chemicals are expensive. In recent years, using low-cost adsorbent for adsorption has been much interested.

Rice husks are agricultural wastes, accounting for about one-fifth of the annual gross rice, 545 million metric tons, of the world. Thailand produces 20-26 million metric tons of rice each year. From this, an estimated 4-7 million metric tons of rice husk are available. The composition of rice husk is: 32.24% cellulose, 21.34% hemicellulose, 21.44% lignin, 1.82% extractives, 8.11% water and 15.05% mineral ash [9]. Typical chemical composition of the mineral ash is: 96.34% SiO₂, 2.31% K₂O, 0.45% MgO, 0.2% Fe₂O₃, 0.41% Al₂O₃, 0.41% CaO and 0.08% K₂O [10]. Rice husk biomass can be exploited for many uses, including: energy production, a mulch [11], production of activated carbon [12], silicon carbide [13] and tetramethoxysilane [14] and as silica for ceramic and Portland cement [15].

Since the main components of rice husk are carbon and silica, it has the potential to be used as an adsorbent. For example, rice husk ash (RHA) produced by heating rice husk at 700 °C has been used as an adsorbent for the removal of lead and mercury [16], and absorb oil on hard surfaces [17]. Rice husk heated at 300 °C has been shown to adsorb more gold-thiourea than the conventionally used activated carbon [18]. Preliminary studies have been shown that RHA was also feasibility for HA removal from water. In the design of improved adsorbents for specific substances, surface modification is very helpful in the improvement of the adsorption capacity and selectivity of the adsorbents by taking advantage of specific interactions between the adsorbents and the adsorbates. Base on these considerations, modification of RHA surface have been regarded as effective adsorbent because of their high surface area which allows the binding of large number of surface groups allow selective adsorption of specific adsorbate.

The present work aims to study the feasibility of using RHA and modified RHA as the adsorbents for the removal of HA. The research accessed the ability of RHA to adsorb HA from synthetic wastewater under different operating conditions, including contact time, pH of solution and initial concentration. Physical and chemical characteristics of RHA were investigated. The comparative efficiency of RHA and commercially activated carbon to adsorb HA was also conducted. Such adsorption system has not been discussed before and no literature data are available in this respect.

Although, Aldrich humic acid is not the best representative of a naturally occurring HA due to the technological isolation/separation procedures, but it was used for the general adsorption evaluation purpose. Even though, the research data presented in this work can serve as a basis and is useful for further applications of the materials in the treatment of water effluents from natural environment.

1.2 Objectives

- (1) To study the rice husk ash preparation methods and the surface modification of rice husk ash for humic acids removal from water.
- (2) To determine the optimum condition for humic acids removal from water.

1.3 Scope of this research

- (1) The preparation of the rice husk ash at 350 and 700 °C and the surface modification of rice husk ash with 3-aminopropyltriethoxysilane (APTS).
- (2) The characterization of adsorbents by the following techniques; elemental analysis (EA), scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and surface area and porosity analysis (BET).
- (3) The determination of the optimum condition for humic acids removal from water by varying the following parameters; contact time, initial pH and initial concentration.
- (4) The comparative efficiency of rice husk ash and activated carbon to adsorb humic acids from water.

1.4 The benefits of this research

To produce a new adsorbent for humic acids removal from rice husk ash in stead of commercially activated carbon. A new adsorbent has advantages over the conventional adsorbents in terms of safety and environmental care.

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CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Humic acids

2.1.1 Chemical composition, structure and properties

Organic matter in the environment can be divided in two main classes of compounds, non-humic material, such as proteins, polysaccharides, nucleic acids, etc. and humic substances. Humic substances are the widest-spread natural polymers on the earth. These brownish biopolymers can be found in sediments, soil and waters. Especially, they are a predominant type of an organic matter in natural waters. The yellowish-brown color of natural water comes from humic substances leached out from plants and soil. Humic substances can affect water quality adversely not only by aforementioned the undesirable color but also in other two ways: complexation with metal ions, yielding in metal ion concentrations exceeding acceptable limits; and second: reaction with chlorine to produce trihalomethanes [2], which are recognized to be human carcinogens. Therefore, it is desirable to minimize the presence of humic substances in drinkable and industrial water. Humic substances can be classified according to their solubility in either acid or alkali and they are operationally defined as follows:

Humic acids: the fraction of humic substances that is not soluble in water under acidic conditions ($\text{pH} < 2$) but is soluble at higher pH values. They are dark brown to black in color.

Fulvic acids: the fraction of humic substances that is soluble in water under all pH conditions. They remain in solution after removal of humic acids by acidification. Fulvic acids are light yellow to yellow-brown in color.

Humins: the fraction of humic substances that is not soluble in water at any pH value. They are black in color.

Many investigators [1-2] now believe that all dark colored humic substances are part of a system of closely related, but not completely identical, high-molecular-weight polymers. According to this concept, differences between humic acids and fulvic acids, can be explained by variations in molecular weight, numbers of functional groups (carboxyl, phenolic-OH) and extent of polymerization.

The postulated relationships are depicted in Figure 2.1, in which it can be seen that carbon and oxygen contents, acidity and degree of polymerization all change systematically with increasing molecular weight. The low-molecular-weight fulvic acids have higher oxygen but lower carbon contents than the high-molecular-weight humic acids. Fulvic acids contain more functional groups of an acidic nature, particularly COOH. The total acidities of fulvic acids (900 - 1400 meq/100g) are considerably higher than for humic acids (400 - 870 meq/100g).

Another important difference is that while the oxygen in fulvic acids can be accounted for largely in known functional groups (COOH, OH, C=O), a high portion of the oxygen in humic acids seems to occur as a structural component of the nucleus.

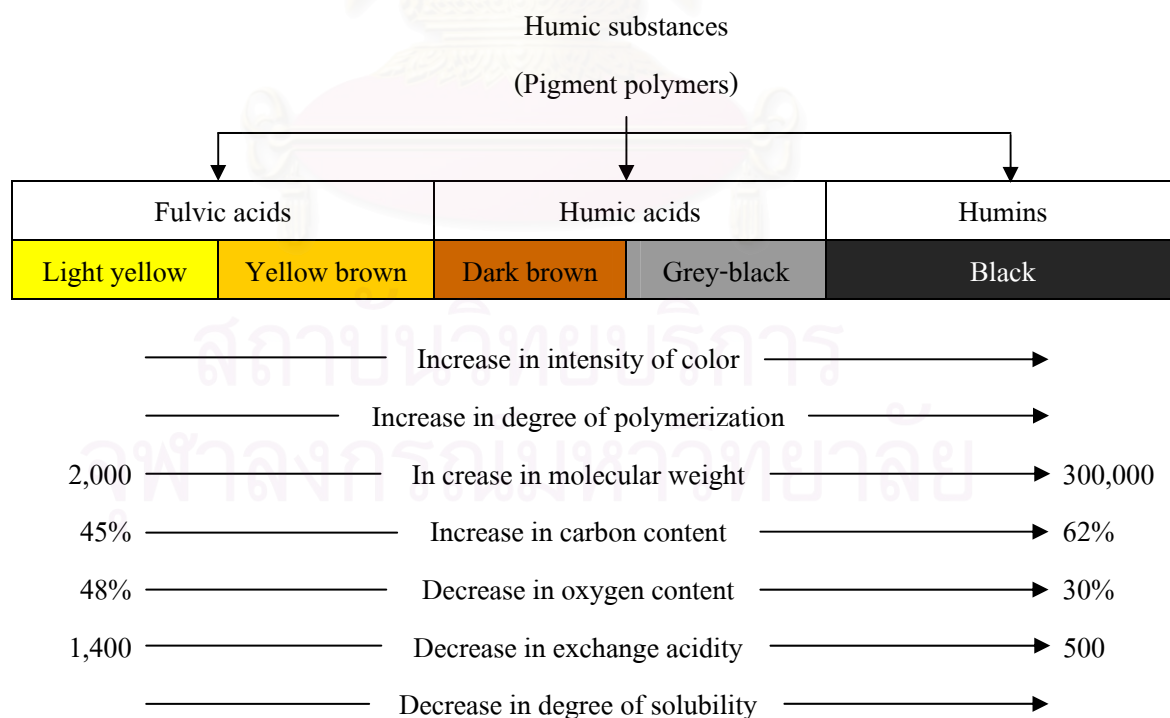


Figure 2.1 Chemical properties of humic substances [19]

2.1.1.1 Elemental composition [20-21]

Humic acids are one of the major components of humic substances which are present in natural waters in concentrations ranging from 20 µg/L in ground waters up to 30 mg/L in surface waters. They are thought to be complex aromatic macromolecules with amino acids, amino sugars, peptides, aliphatic compounds involved in linkages between the aromatic groups. The compositions of humic acids vary with the nature of the original organic material, the conditions which prevail during the decomposition, method of extraction, and other parameters. The elemental compositions of representative water and soil humic acids are given in Table 2.1.

Table 2.1 Summary of elemental compositions of humic acids (HA) extracted from tropical and temperate region soils and miscellaneous environments (the figure are averages of weight percentages from multiple analyses of various sources) [22]

	C	H	O	N	S	C/N
	-----		%	-----		
Tropical region soils						
HA-Alfisol	52.3	5.2	37.2	3.6	n.d	14.5
HA-Andosol	58.5	3.9	34.8	3.8	0.3	15.4
HA-Oxisol	54.5	4.4	38.0	3.1	n.d	14.5
Temperate region soils						
HA-Alfisol	56.8	5.0	33.6	4.6	n.d	12.3
HA-Ardisol (Solonetz)	54.5	4.1	36.4	5.0	n.d	10.9
HA-Histosol (Peat-bogs)	58.7	5.0	32.9	3.4	n.d	17.3
HA-Inceptisol	51.4	5.4	39.1	4.1	n.d	12.5
HA-Mollisol	53.7	4.3	36.3	3.7	n.d	14.5
HA-Spodisol	53.1	4.9	39.2	3.5	0.4	15.2
HA-Ultisol	50.5	5.2	40.0	3.9	0.5	12.9
Geologic deposits						
Lignite	52.6	2.8	31.8	2.0	0.7	26.3
HA-lignite	57.4	3.9	36.8	1.2	0.8	47.8

n.d = not determined

Table 2.1 (con.)

	C	H	O	N	S	C/N
	-----		%	-----		
River and swamps						
HA-aquatic	49.6	4.8	43.5	2.1	n.d	23.6
Merck chemical. Co.						
HA-artificial	59.8	4.8	33.6	1.8	n.d	33.2

n.d = not determined

2.1.1.2 Functional group composition [20-21]

The functional groups are composed of a set of active chemical groups that give the humic acids their unique chemical behavior. Interaction reaction characteristics for humic acids, e.g., complex formation, chelation, and ion or metal bridging, are attributed to their presence in the humic molecule.

These groups are sometimes referred to by different names. Stevenson [19] suggested naming them *oxygen containing functional groups*, though some of the groups do not contain oxygen at all. In contrast, Purdue [23] preferred to call them *acidic functional groups*, which also limit the groups to units that behave acidic only. The major types of functional groups are in the form of COOH, phenolic-OH, alcoholic-OH, and carbonyl groups. These units indeed contain oxygen atoms. In addition to the above, amino groups are also important functional groups, but these are neither of the oxygen containing nor of the acidic types.

Carboxyl groups: the carboxyl or COOH groups give acidic characteristic to the humic molecule and make humic acids exhibit property changes, and have the capacity to adsorb and exchange cations. As can be noticed in Figure 2.4 these carboxyl groups will dissociate their H atoms at pH 3.0. A summary of the average values of COOH, phenolic-OH contents, and total acidity in humic acid is provided in Table 2.2

Hydroxyl groups: humic acids contain a variety of hydroxyl groups, but for characterization of humic acids generally three major type of OH groups are distinguished:

- Total hydroxyls: they are the OH groups which associated with all functional groups, such as phenols, alcohols and hydroquinones but refer only to the sum of phenolic- and alcoholic- OH groups.

- Phenolic hydroxyls: they are the OH groups which attached to aromatic structures. There is no chemical method for the determination of these groups. The phenolic-OH group is usually determined by difference as follows:

$$\text{meq phenolic-OH} = \text{meq total acidity} - \text{meq COOH} \quad (2.1)$$

- Alcoholic hydroxyls: they are the OH groups associated with alcoholic groups or non-aromatic carbon. The amount can also be determined by difference only:

$$\text{meq alcoholic-OH} = \text{meq total OH} - \text{meq phenolic-OH} \quad (2.2)$$

Total acidity: this is not a functional group (a very important characteristic of humic acids closely related to the functional groups). It is commonly used as a measure for the cation exchange capacity of humic acids. Though can be determined by titration method which is calculated by summation as follows:

$$\text{meq total acidity} = \text{meq COOH} + \text{meq phenolic-OH} \quad (2.3)$$

Table 2.2 Summary of COOH, phenolic-OH contents, and total acidity in soil, geologic, and aquatic humic acids [20]

	Carboxyl	Phenolic hydroxyl	Total acidity
	----- meq/g -----		
Soil			
HA-Alfisol	3.9	2.8	6.8
HA-Inceptisol	2.4	3.6	6.0
HA-Spodisol	5.4	3.5	8.9
HA-Ultisol	3.7	4.4	8.1
Geologic Deposit			
HA-lignite	5.2	0.9	6.1
Rivers and swamps			
HA-aquatic	3.4	2.5	5.9

2.1.1.2 Molecular structure

The molecular structure is not possible to integrate all of the compositional data into neat structural models for humic acids because of its environmental influences. For example, humic acids with the greater oxygen content will have a greater concentration of functional groups. This composition will be likely to cause the humic acids to be more hydrophilic, and consequently less effective in the uptake of nonionic compounds. However, the higher concentration of oxygen-containing functional groups will likely render them more acidic and more effective in complexing metal ions.

Stevenson suggested on molecular structures are based on aromatic constituents or phenols obtain by variety of degradation analyses of humic acids. The hypothetical structure for humic acid, shown in Figure 2.2, contains free and bound phenolic OH groups, quinone structures, nitrogen and oxygen as bridge units and COOH groups variously placed on aromatic rings.

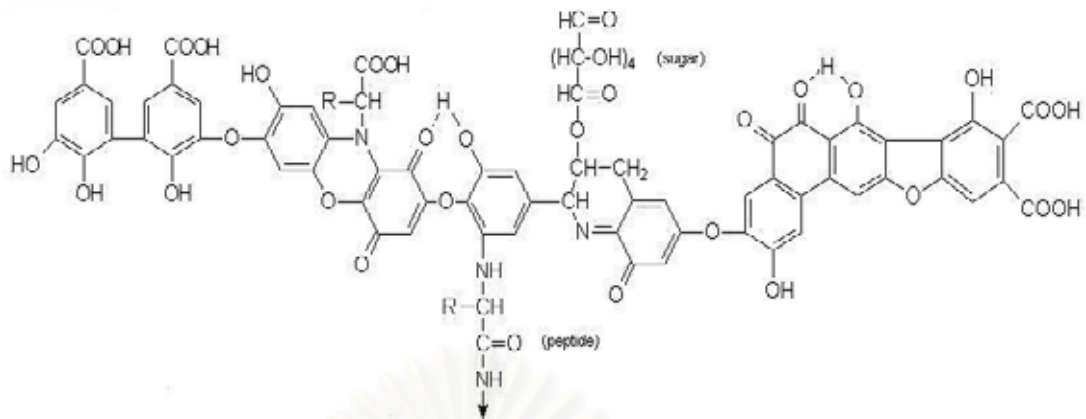


Figure 2.2 Model structure of humic acid based on aromatic constituents [19]

2.1.1.3 Electrochemical properties [20, 24-26]

Humic acids are considered amphoteric compounds, but Stevenson [19] assumed them to be weak acid. However, it is well known that humic acids can react with both bases and acids, hence carry both positive and negative charges. These properties and behavior are regarded as distinctive characteristics of amphoteric substances. The negative charges are usually studied more intensively and consequently are better known than the positive charges. All these charges are developed by the ionization or dissociation of various functional groups.

- *Negative charges*

The negative charges are attributed to dissociation of protons from the functional groups in the humic molecule. The two most important functional groups in this respect are the carboxyl and phenolic-OH groups. In general, these two functional groups control the electrochemical behavior of humic acids and are the main reasons for adsorption, cation exchange, complex and chelation reactions. The carboxyl, COOH, groups start to dissociate their protons at pH 3.0 and the humic molecule becomes negatively charged (Figure 2.3). At pH < 3.0, the charge is very small, or even zero. At pH 9.0, the phenolic-OH groups also dissociate their protons, and the humic molecule attains a high negative charge.

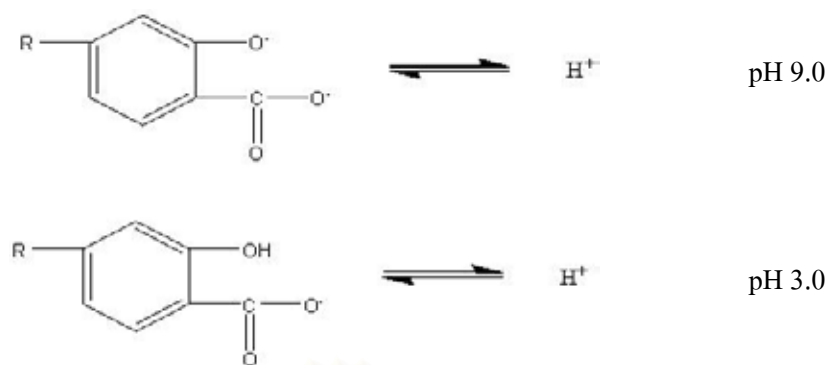


Figure 2.3 Development of variable of changes in humic molecule by dissociation of protons from carboxyl groups at pH 3.0, and from phenolic-OH groups at pH 9.0

- Positive charge

The positive charges are caused by the presence of amino groups. Protonation of amino groups will create positive charges. By comparison with the oxygen-containing functional groups, the concentration of amino groups in humic acids is often believed to be relatively small. This is perhaps one of the reasons why the positive charges of humic acids are considered to be only of minor importance.

2.1.2 Determination of humic acids in water samples

The presence of humic acids in water intended for potable or industrial use can have a significant impact on the treatability of that water and the success of chemical disinfection processes. Accurate methods of establishing humic acids concentrations are therefore essential in maintaining water supplies, especially from upland peaty catchments in temperate climates.

As a lot of different humic molecules in very diverse physical associations are mixed together in natural environments, it is difficult to measure their exact concentrations and allocate them to a certain class of bio-organic molecules. For this reason concentrations of humic acids classes can be estimated out of concentrations of organic matter (typically from concentrations of total organic carbon; TOC or dissolved organic carbon; DOC).

UV-visible spectrometry has also been conventionally proposed to characterize dissolved organic matter in the watercourses. Most research has employed the measurement at the wavelength of 253.7 nm (often rounded off to 254 nm) as the representative for the relative quantity of aromatic-humic substances [27]. Usually the Beer-Lambert law is employed to determine the concentration of humic acid in solution from a measurement of absorbance at wavelength of maximum absorption humic acids.

2.1.3 Environmental effects [21, 25]

Despite the importance of humic acids regarding soil fertility, its presence in the environment can be a problem due to the formation of the complex HA-metal ions which leads to metal transportation and release in soil. However, one of the major concerns for the environmental problem caused by the presence of humic acids in waters that will undergo chlorine treatment for human population consumption. This may result in the formation of disinfection by-products (DBPs) such as trihalomethanes (THMs) and halo acetic acids (HAAs) that are carcinogenic products and have their presence limited to 100 ppb in potable water by the World Health Organization (WHO) [28].

2.1.4 Influences of humic acids on water treatment process [21]

The presence of humic acids in water has long been a problem for the water supply industry. Major problems result from the fate that humic acids:

- (1) produce esthetically undesirable problems such as color in the water;
- (2) serve as precursors of potentially hazardous trihalomethanes during chlorination processes;
- (3) act as precursors of other low- and high-molecular-weight chlorine-containing organic compounds that are produced during chlorination;
- (4) serve as precursors of low- and high-molecular-weight organic compounds that are formed by oxidation during ozonation processes;
- (5) stabilize dispersed and colloidal particles during coagulation processes;

- (6) lead to the formation of biodegradable organic compounds during ozonation and thereby enhance regrowth of microorganisms within the water distribution systems;
- (7) can compete with pollutant compounds for adsorption sites in activated carbon adsorption; and
- (8) can precipitate in the distribution system; this precipitation can lead to deterioration of tap water quality and increase the need for interior cleaning of pipes.

Water treatment processes have been designed primarily to remove pathogens and turbidity through the use of coagulation, flocculation, sedimentation, filtration and disinfection with ozone and chlorine processes. As is true in any serial set of processes, the efficiency of the first (coagulation) process will affect subsequent processes. Because humic acids stabilize dispersed and colloidal particles, the removal of humic acids has been a focus of the coagulation process.

During coagulation, stabilization of dispersed and colloidal particles can occur through the adsorption of the higher-molecular-weight humic acids on the surface of the mineral particles. A strong interaction has often been observed between the dissolved humic acids and the flocculants. In most cases, higher humic acids concentrations mean larger flocculant dosages and therefore higher treatment cost.

An alternative to coagulation for particle removal during water treatment is membrane filtration. The main problem with membrane filtration is irreversible fouling of the membrane by complex mixtures of inorganic materials and humic acids.

Chlorine can combine with humic acids in water to form chlorinated organic compounds, such as chloroform, other low-molecular-weight disinfection by-products (e.g., haloacetonitriles, haloacids, haloaldehydes, haloketones, chlorophenols, chloropicrin, and cyanogens chloride) and complex high-molecular-weight chlorinated compounds. All of these compounds may have adverse effects on human health.

Oxidation processes also can change the chemical structure of humic acids and alter the biodegradability of these compounds. In German waterworks, ozonation is very often used to render humic acids from surface water more biodegradable. However, the biodegradable compounds need to be removed before entering the water distribution system, where they can enhance regrowth of microorganisms.

Background dissolved organic carbon (DOC) can also influence the treatment of pollutants by reducing the capacities and rates of the carbon adsorption unit processes for the removal of smaller molecules that present a known health hazard. Thus, the lower concentration of humic acids presented in the influent water to the activated carbon contactor, the more efficient process will be for pollutant removal.

2.1.5 Conventional methods for removal of humic acids

As the humic acids are the main precursors for chlorinated by-products. Controlling the THMs formation could then be accomplished by lowering the precursors in the water before chlorination. Several methods for the removal of humic acids in the water sources were reviewed and summarized below.

2.1.5.1 Adsorption with activated carbon

Humic acids could be well adsorbed on the surface of activated carbon (AC). Granular activated carbon (GAC) and powder activated carbon (PAC) are often used in drinking water treatment for the removal of organic, odor, taste, and color. Activated carbon can remove organic precursors effectively with an adequately long contact time provided that adsorption capacity is high.

2.1.5.2 Membranes

There are several types of membranes used for treating water supply treatment; microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). The pore sizes of the membranes could be ordered from large to small as follows; MF > UF > NF > RO.

MF and UF are not very good in humic acids removal because of their large pore size. Smaller pore membranes such as NF and RO can significantly remove humic acids.

2.1.5.3 Anion exchange

Generally, humic acids in water at neutral to basic pH range is present as negative ions so it can be removed by anion exchange resin. Bolto et al. [29] explored an anion exchange for the removal of humic acids and report that ion exchange was an effective method for removing humic acids in water.

2.1.5.4 Coagulation and sedimentation

Conventional water treatment facilities generally consist of coagulation, sedimentation, and filtration process, which have been traditionally used to remove suspended solids for drinking water. These processes, although might not be effective, could also remove organic contaminants in the water. With a proper control of coagulation condition, several reports have shown that some specific trihalomethanes precursors could be removed. The removal of disinfection by-products (DBPs) precursors represents a valuable option for reducing the potential for chlorinated by-products formation without requiring significant capital investments, As coagulation is among the most economical means employed in the water treatment facilities, it has been received considerable attention as a method for removing THM precursors and has been proposed as the best available technology of the stage 1 of the D/DBP Rule [30]. Note that enhanced coagulation included the proper usage of coagulant aids and the adjustment of the pH of raw water.

2.2 Disinfection and disinfection by-products

Disinfection is used to eliminate pathogenic microorganisms in drinking water and also sewage effluent. Pathogens presented in water supplies are extremely harmful and can cause diseases in humans. For drinking water, disinfection is an important step to ensure that water is safe to drink, and the U.S. regulation (Environmental Protection Agency, EPA) stated that disinfection must provide a 99.99 percent inactivation of *Giardia lamblia* and enteric viruses to

protect human health. Moreover, a certain level of disinfectant should remain in the finished water to prevent the regrowth of microorganisms in the distribution system.

2.2.1 Disinfectants

Disinfection can be achieved with many chemical disinfectants such as ozone, ultraviolet (UV) radiation, potassium permanganate, chlorine dioxide, and chlorine. Each method has its own advantages and disadvantages as briefly discussed below.

- *Ozone*

Ozone is the most effective oxidant and disinfectant. It is formed by passing air through high voltage electrical discharge field where O_2 is converted to O_3 . As a very strong oxidant, ozone requires shorter contact time and lower dose than most other disinfectants. However, as ozone is unstable, it is required that ozone be generated on-site which means that every facility must have an ozone generator. In addition, ozone cannot remain long enough in the water distribution system and therefore this poses the problems on the reproduction of the microorganisms.

- *Ultraviolet radiation*

Ultraviolet (UV) radiation is generated by a specific lamp. When the radiation penetrates through the cell wall of an organism, the cell's material is interrupted and the cell is incapable of further reproducing. UV light is an effective disinfectant particularly to destroying bacteria and viruses. The efficiency depends on the contact time. However, it cannot provide a disinfecting role in the water distribution system. UV radiation is unsuitable for water with high levels of suspended solids, color, turbidity, or soluble organic matter because these materials can adsorb and obstruct the UV radiation which leads to a lower disinfection performance.

- Chlorine dioxide

Chlorine dioxide (ClO_2) is a very effective disinfectant for odor and taste control but it has so be generated onsite because chlorine dioxide is an unstable gas. This gas was reported to produce only few disinfection by-products of concern which are chlorite and chlorate. There is no significant formation of trihalomethanes and it dose not react with bromide to form brominated by-products.

- Chlorine

At atmospheric pressure, chlorine gas is toxic, yellow-green in color, and forms liquid at high pressure. Chlorine is most widely used in the disinfection process because it is very effective for removing almost all microbial pathogens. It is appropriate as most primary and secondary disinfectants. Moreover, the most important advantage that chlorine still commonly using is it can maintain as a residual disinfectant in the water supply distribution system. However, the formation of DBPs can occur.

2.2.2 Disinfection by-products

Disinfection by-products (DBPs) can form when disinfectants, such as chlorine, react with naturally present compounds in water. The formation of these products mainly takes place during reactions in which organic substances, such as humic acids and fulvic acids. These materials end up in water during the natural decomposition of plant matter.

In 1971, the American scientist Bellar discovered that chloroform was absent in the Ohio river water which was used for drinking water production. However, chloroform appeared to be present in drinking water originating from drinking water purification plants. This proves the formation of DBPs during chlorination.

Little information can be found on the chemical structures of humic acids and fulvic acids. The mechanism of formation of DBPs therefore remains unclear. Research is difficult,

because of the extensive number of substances that make up organic matter. A variety of DBPs are described below.

- Ozone disinfection by-products

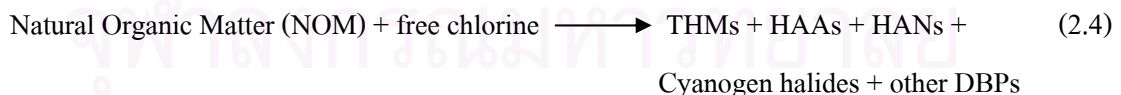
Ozone will not produce chlorinated by-products such as trihalomethanes, haloacids (HAAs), and haloacetonitrils but it may form a variety of the oxidation by-products in the presence of organic matter [31]. However, if the water contains bromide ions are ozonated, bromide species DBPs can form.

- Ultraviolet radiation disinfection by-products

It is possible to obtain oxidative by-products in the high pressure UV systems. UV DBPs may form due to the production of OH radicals when the water is in contact with UV radiation. However, conventional UV dose not appear to form any DBPs of current concerns [32].

- Chlorine disinfection by-products

Chlorine DBPs are formed when free chlorine (hypochlorous acid: HOCl) added to water reacts with the organic matter presented in water. THMs were often found to be the most dominant DBPs, follow by HAA. THMs and HAAs were identified as potential adverse health effect agents. The generalized equation describing the formation of chlorine halogenated DBP is shown in Equation 2.4.

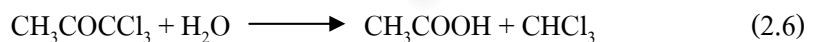
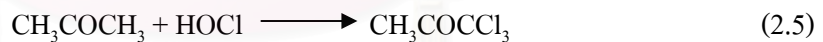


2.2.3 Trihalomethanes

Trihalomethanes (THMs) are organohalogen compounds which are the derivatives of methane when three out of the four hydrogen atoms are substituted by three halogen atoms such as chlorine, bromine, and iodine. THMs species of concerns in drinking water are chloroform, bromodichloromethane, dibromochloromethane, and bromoform. The chemical structures of these THMs species are listed in Table 2.3

THMs were found in chlorinated drinking water since 1974 by Rook [33]. THMs have been shown to potentially cause tumors in liver, kidney or large intestine in laboratory animals. Chloroform is often used as a representative of the THMs because it usually presents in the greatest concentration among the four THMs species. Chloroform is also commonly used in chemical and pharmaceutical industries. National Cancer Institute of the United States showed that chloroform increased mouse liver tumors and increased kidney tumors in rats. National Toxicity Program, Department of Health and Human Services of the United States reported that bromodichloromethane induced renal tumors in mice and rats, liver tumors in mice and intestinal tumors in rats whereas bromoform produced intestinal tumors in rats [34].

Reaction mechanism:



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Table 2.3 Common trihalomethanes (ordered by molecular weight)

Molecular formula	IUPAC name	Common name	Other names
CHF ₃	trifluoromethane	fluoroform	Freon 23, R-23, HFC-23
CHClF ₂	chlorodifluoromethane	-	R-22, HCFC-22
CHCl ₃	trichloromethane	chloroform	methyl trichloride
CHBrCl ₂	bromodichloromethane	-	-
CHBr ₂ Cl	dibromochloromethane	-	-
CHBr ₃	tribromomethane	bromoform	methyl tribromide
CHI ₃	triiodomethane	iodoform	methyl triiodide

In the United States, the standard was reduced from 100 to 80 µg/L in the “Stage 1 disinfectants and disinfection by-product rule”. The WHO has a separate standard considering THM: bromine dichloromethane (BDCM) 60 µg/L, bromoform 100 µg/L and chloroform 200 µg/L.

2.2.4 Halogenic acetic acids

Halogenic acetic acids (HAAs) are an important type of chlorinated DBPs. Acetic acids consist of three hydrogen atoms that are fixed to a COOH-group. H-atoms of HAA are partly replaced by halogen atoms. HAAs are non-volatile compounds. HAA can occasionally be found in the water. When the pH value is lower, more HAAs are formed and when the pH value is higher, more THMs are formed. The composition of naturally present organic matter also determines the amount of THMs or HAAs that is formed.

Like THMs, HAAs concentrations in surface water in summer exceed concentrations in winter and surface water contains more HAAs than groundwater. HAAs contribute to THMs formation; during the biological decomposition of HAAs, THMs are formed. When pH values are low, trichloropropanone is oxidized further to form tetra-, penta-, and hexachloropropanone.

When these compounds are hydrolysed, mono-, di-, and trichloro acetic acids will form. HAAs are suspected to raise the risk of cancer.

Reaction mechanism:



In the United States, the EPA has established a standard of 80 µg/L for HAAs. The WHO does not dictate any standards for HAAs.

2.2.5 Haloacetonitriles

Haloacetonitriles (HANs) are drinking water contaminants produced during chlorine disinfection. These chemicals are usually present in lower amounts than THMs and HAAs, and formed immediately during water disinfection but are decomposed quickly during hydrolysis reactions or reactions with residual disinfectants. The compounds cannot be formed at high pH values.

HANs are formed during a reaction of chlorine and acetonitrile. These DBPs are decomposed when the reaction time of the disinfectant in the water is low. Trichlorine acetaldehyde and brominated aldehyde compounds are the second largest group of DBPs imaginable. Mono- and dichlorine acetaldehyde can be formed during disinfection, but will immediately be oxidized to form trichlorine acetaldehydes. Acetaldehyde is a DPB of ozone disinfection. When ozone is combined with chlorine, trihaloacetaldehydes form.

Reaction mechanism of acetaldehyde and chlorine:



2.2.6 Standards for disinfection by-products

Some DBPs are considered harmful for public health (chloroform, dibromochloromethane and bromoform are probably carcinogenic and dichlorobromomethane, dichloroacetonitrile and chloral hydrates are possibly carcinogenic). Health institutions worldwide have set standards for the maximum concentration of DBPs in drinking water.

In the European Drinking Water Directive 98/83/EC the maximum standard for THMs is set to 100 µg/L. If possible countries should strive for lower concentrations. The WHO describes separate standards for three THMs: bromodichloromethane (BDCM) 60 µg/L, bromoform 100 µg/L, and chloroform 200 µg/L. The EPA is concerned with regulation on DBPs in the United States since 1979. In 1996 the Safe Drinking water Act was revised and the Congress asked USEPA to set new standards for disinfectants and DBPs. This revision aims at lowering the health risk of DBPs, while protecting microbiological quality of the water. In 1998, EPA promulgated the *Stage 1 Disinfectants and Disinfection By-products Rule*. The standard on total trihalomethane concentration is 80 µg/L and for halogenated acidic acid 60 µg/L. The guideline also states that advanced coagulation must be used to remove organic matter. The Metropolitan Waterworks Authority of Thailand describes separate standards for four THMs: chloroform 200 µg/L, bromodichloromethane 60 µg/L, dibromochloromethane 100 µg/L, and bromoform 100 µg/L [35].

2.3 Rice husk and rice husk ash

2.3.1 Properties of rice husk

The beneficiation of rice generates as by-product rice husk that corresponds to about 23% of its initial weight. This husk can be used as a fertilizer in agriculture [36] or as an additive for cement and concrete fabrication [37]. The compositions of rice husk are cellulose, lignin, small quantities of proteins and vitamins, inorganic compounds rich in silicon and small concentration of other metals [38]. The quantity of each composition depends on the soil type, plant variety and climate condition, etc. Figure 2.4 shows SEM micrographs of rice husk [39].

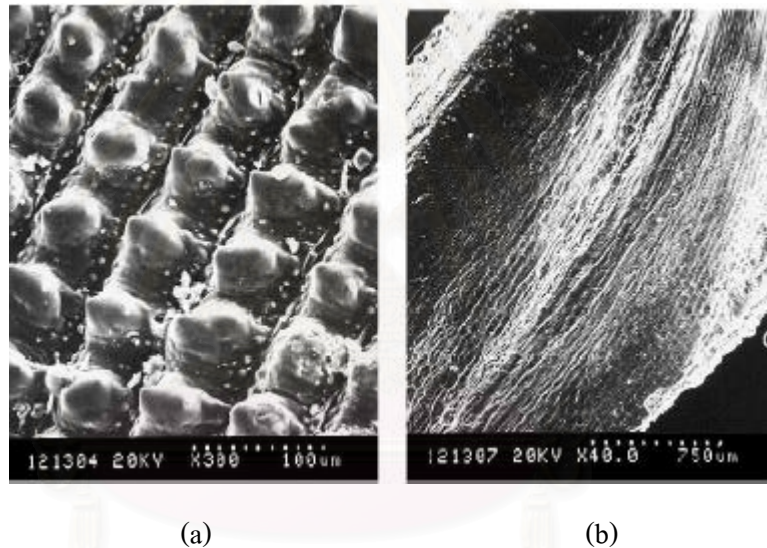


Figure 2.4 Scanning electron micrographs of rice husk: (a) outer epidermis of rice husk; (b) inner epidermis of rice husk

The outer surface of rice husk was highly ridged structure has a linear profile. Silica is mainly localized in the tough interlayer of rice husk and also filling in the space between the epidermal cells. The physical and chemical properties on analysis data of rice husk are shown in Table 2.4.

Table 2.4 Rice husk analysis data [39]

Proximate analysis		(by mass)
Moisture		6%
Ash		16.92%
Volatile		51.98%
Fixed carbon		25.10%
Ultimate analysis		
Carbon		37.60%
Hydrogen		4.89%
Sulfur		0.01%
Nitrogen		1.89%
Oxygen		32.61%
Ash		16.92%
Gross calorific value		13.4 MJ/kg
Physical properties		
Diameter range		0-10 mm
Equivalent mean diameter		1.60 mm
Natural packing density		122 kg/m ³
Real density		500 kg/m ³

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2.3.2 Properties of rice husk ash

Rice husk ash (RHA) is obtained by burning the rice husk and in particular in plants where rice milling is performed with cogeneration or similar facilities or in plants for the production of parboiled rice. In general, the RHA so obtained is dumped as a waste. Globally, approximately 600 million tones of rice paddy are produced each year. Assuming a husk to paddy ratio of 23%, and a ash to husk ratio of 18% [40], the total global ash production could be as high as 21,000,000 tones per year. RHA is a general term describing all types of ash produced from burning rice husks. In practice, the type of ash varies considerably according to the burning technique.

The presence of silica (SiO_2) in rice husk has been known since 1983 [41]. Rice husk produce a high ash content, varying from 13 to 29 wt% depending on the variety, climate, and geographic location. The ash is largely compost of silica (87 to >99%) with small amounts of inorganic salts. Other literatures (Armesto et al. [42] (87.7% as SiO_2); Liou [43] (>90% silica); Kapur [44] (>95% silica); Houston [45] (87 to 97% silica); and Yalcin et al. [12] (>99% as SiO_2)) consistently reported that RHA contains very high silica content. The silica in the rice husk exists in the hydrated amorphous form like silica gel. Due to its high silica content rice husk has become a source for preparation of a number of silicon compounds such silicon carbide [46], silicon nitride [47], sialon and zeolite [48]. Silica ash obtained by calcining rice husk is also used in the cement industry. Rice husk silica has fine particle size and high reactivity and has been used in the production of activated silica, sodium silicate, potassium silicate and solar grade silicon [49].

Many authors [50-51] have concluded that preliminary leaching of rice husk with a solution of HCl, HNO_3 , H_2SO_4 , NaOH and NH_4OH , boiled before thermal treatment with temperatures ranging from 500 to 1400 °C for various time intervals [52], proved to be effective in substantially removing most of the metallic impurities and producing ash silica completely white in color with a high specific surface area. Figure 2.6 shows SEM micrographs of RHA.

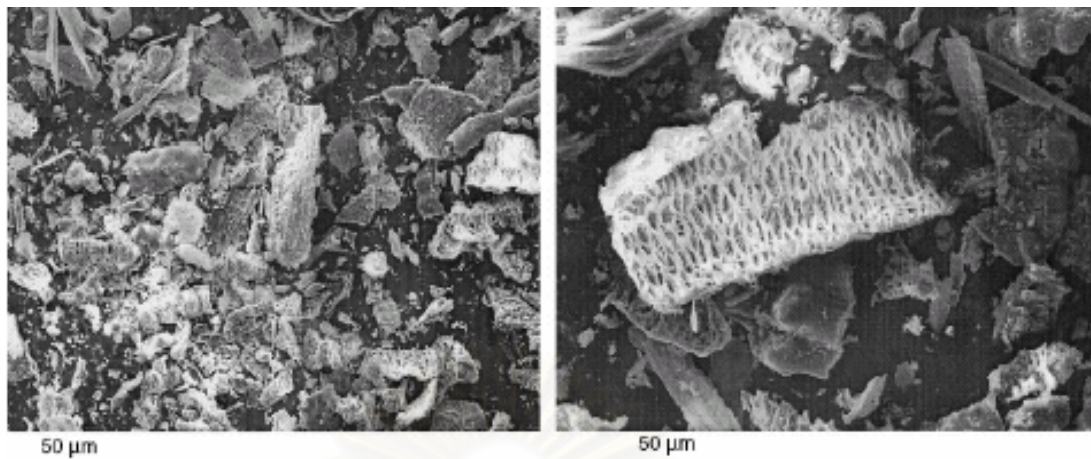


Figure 2.5 Scanning electron micrographs of rice husk ash [39]

The SEM micrographs of RHA (Figure 2.5) reveal its surface texture and porosity. It shows very fine particle size to the order of a millimeter or less and that there are pores of vary sizes within the particle. The chemical composition on analysis data of RHA are shown in Table 2.5

Table 2.5 Chemical composition of RHA after burning at 700 °C for 6 h [12]

Components expressed as oxides	wt%
SiO ₂	94.95
Al ₂ O ₃	0.39
Fe ₂ O ₃	0.26
CaO	0.54
Na ₂ O	0.25
K ₂ O	0.94
MnO	0.16
TiO ₂	0.02
MgO	0.90
P ₂ O ₅	0.74
Loss on fire	0.85

Silica in rice husk was amorphous in nature, as indicated by a broad peak centered on 2θ angle of 22° in Figure 2.6. However, at high temperature for a prolonged period of time (Figure 2.7), the cristobalite form of silica in the rice husk will transform into crystalline form. The crystallisation of silica in the rice husk ash is characterized first by the formation of the cristobalite crystals and then the tridymite crystals. The formation of cristobalite could be explained as follows [53]: (i) Si–O bonds are liberated from the long polymeric chains (Si–O–C/Si–O–Si) at elevated temperatures. (ii) Subsequent cooling of the Si–O bonds has little or no tendency to crystallise. (iii) When the pyrolysis temperatures are increased, more and more Si–O and C–O/C–C are released, which gradually transform to crystalline silica (cristobalite) and crystalline carbon (graphite).

The minimum temperature for the onset of crystallization of silica in rice husk ash into cristobalite was reported to be 700°C [54-58]. Other literatures reported even higher temperature limits, such as 800°C [59-61] and 900°C [62-65]. The formation of tridymite, meanwhile, only starts at temperature approximately 1000°C and become more prominent at temperatures beyond 1200°C [66].

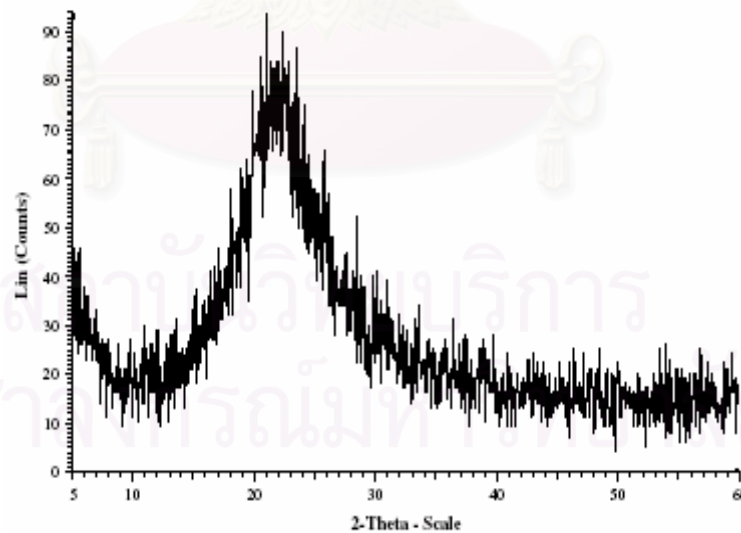


Figure 2.6 Diffractogram of rice husk ash in nature [39]

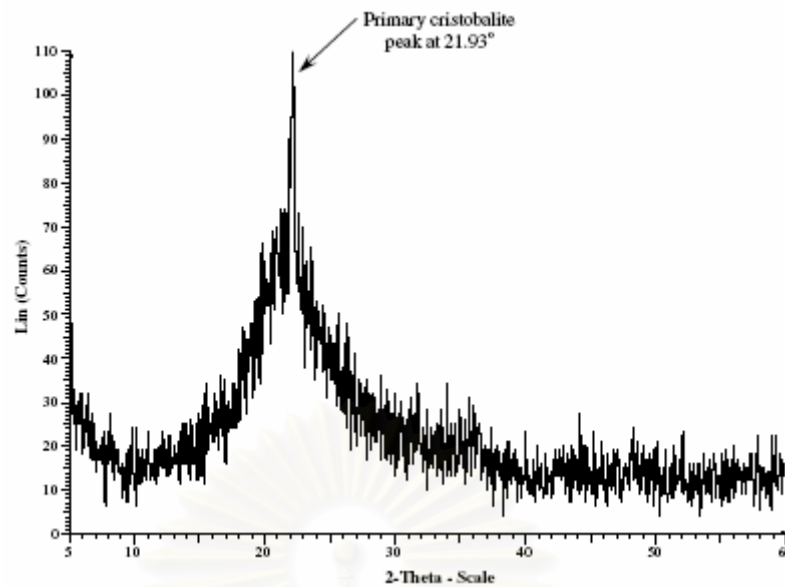


Figure 2.7 Diffractogram of crystallised rice husk ash (presence of cristobalite peak) [39]

Yalcin and Sevinc [12] reported that, by acid leaching, silica of > 99% purity can be obtained by burning rice husks at 700 °C and the specific surface areas reached ~260 m²/g. The BET specific surface areas are given in Table 2.6. The RHA with small particle size and high specific surface area can be use with different aims, for instance, an adsorbent or catalyst support.

Table 2.6 BET specific surface area and specific pore volume of rice husk ash

Treatment	Specific surface area (m ² /g)	Pore specific volume (cm ³ /g)	Average pore diameter (µm)
-	63	-	-
HCl	321	4.7297	0.0045
Distilled water	194	-	-
H ₂ SO ₄	282	-	-
HCl (Pre- and post-)	244	-	-

Previous literatures indicated that the RHA has the potential to be used as an adsorbent for the removal of the pollutants from water. For example, RHA produced by heating rice husk at 700°C has been used as an adsorbent for the removal of lead and mercury [16], metal ions [67], Brilliant Green dye from aqueous solution [68] and absorb oil on hard surfaces [17]. Rice husk heated at 300°C has been shown to adsorb more gold-thiourea than the conventionally used activated carbon [18].



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2.4 Adsorption

2.4.1 Principles of adsorption

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (adsorbate). It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. The term sorption encompasses both processes, while desorption is the reverse process (Figure 2.8).

Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification. Adsorption, ion exchange and chromatography are sorption processes in which certain adsorptives are selectively transferred from the fluid phase to the surface of insoluble, rigid particles suspended in a vessel or packed in a column.

Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be they ionic, covalent or metallic) of the constituent atoms of the material are filled. But atoms on the (clean) surface experience a bond deficiency, because they are not wholly surrounded by other atoms. Thus it is energetically favorable for them to bond with whatever happens to be available. The exact nature of the bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting physisorption or chemisorption.

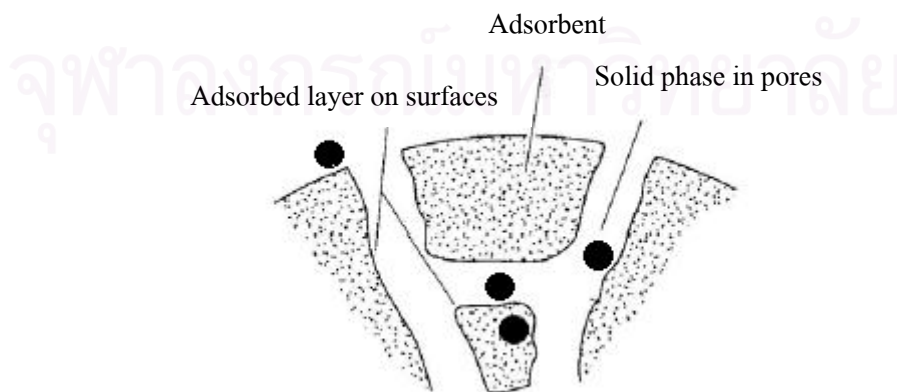


Figure 2.8 Adsorption operation with solid-particle adsorbents

2.4.1.1 Physical adsorption

Physical adsorption (physisorption) is a result of intermolecular forces that interact between the adsorbate and the adsorbent. These physical electrostatic forces include the van der Waals force, consisting of weak attraction and repulsion through dipole-dipole interactions and dispersing interactions, and hydrogen bonding. Dipole-dipole interactions are the result of polar compounds orienting themselves so that their charges result in the lower combined free energy. Dispersing interactions are the result of attractive forces between electron and nuclei of molecular systems. If the molecules come too close to each other, repulsive forces can pull the molecule apart. Hydrogen bonding is a special case of dipole-dipole interaction in which the hydrogen atom in molecule has a partial positive charge, attracting another atom or molecule with a partial negative charge. For liquid phase systems, the van der Waals force is the primary physical force driving interaction. Physical force interaction is a readily reversible reaction and includes both mono- and multilayer coverage. Because physical adsorption does not involve the sharing of electrons, it generally has low adsorption energy, and is not site specific. The heat of adsorption for the reaction is on the order of 40 Btu/lb per mole of the adsorbate. When the intermolecular forces between a chemical molecule in liquid stream and a solid (the adsorbent) are greater than the forces between the molecules of liquid stream, the chemical is adsorbed onto the adsorbent surface.

2.4.1.2 Chemical adsorption

Chemical adsorption (chemisorption), like physical adsorption, is also based upon electrostatic forces. The mechanisms of chemical adsorption are similar to those of physical adsorption, yet are often stronger (approaching the adsorption energies of chemical bonds). The transfer of electrons and the formation of chemical bonds between the adsorbate and the adsorbent produce chemical adsorption. It may be an irreversible reaction and have high adsorption energies. The heat of adsorption is significantly greater than for physical adsorption, ranging from 80 to 400 Btu/lb per mole of the adsorbate. It is not unusual for the adsorbate to have chemically changed due to the reaction. Chemical adsorption involves only monolayer coverage, and is a site specific reaction, occurring at specific functional group locations.

Functional groups are distinctive arrangements of atoms in organic compounds that give that compound its specific chemical and physical properties.

Table 2.7 Distinction between physical adsorption and chemical adsorption

Characteristics	Physical adsorption	Chemical adsorption
Heat of Adsorption /kJmol ⁻¹	20 - 40 c.f. heats of liquefaction	> 80 c.f. bulk-phase chemical reactions
Rate of Adsorption (at 273K)	Fast	Slow
Temperature Dependence of Uptake (with Increasing T)	Decreases	Increases
Desorption	Easy- by reduced pressure or increased temperature	Reversible Difficult - high temperature required to break bonds
Specificity	Non-specific	Very Specific
Monolayer Coverage	Mono or multilayer condition dependent	Monolayer

Adsorption onto solid adsorbent has great environmental significance, since it can effectively remove pollutants from aqueous streams. Due to the high degree of purification that can be achieved, this process is often used at the end of a treatment sequence.

2.4.2 Mechanism of adsorption onto the porous adsorbent [69]

For the adsorption of the solute onto the porous surface of an adsorbent, these are essentially four stages in the adsorption process, the following steps are required;

- (1) transport of the solute from the bulk of solution to the exterior surface of the adsorbent;
- (2) movement the solute across the interface and adsorption onto external surface sites;
- (3) migration of the solute molecules with in the pores of the adsorbent; and

- (4) interaction of the solute molecules with the available sites on to the interior surfaces, bounding the pore and capillary spaces of the adsorbent.

2.4.3 Factor effecting of humic acids adsorption

As a generalization, the adsorption capacity of given adsorbent material is proportional to the surface area available. However, there are a number of other factors that affect adsorption.

2.4.3.1 Surface area and pore size distribution

One of the major considerations when selecting the adsorbent is the surface area of the material. Adsorbent materials used for wastewater treatment are highly porous. The majority of the surface area of rice husk ash is provided by the pore structure. Another surface area property affecting adsorption is the distribution of pore size diameters.

Pore size distribution is a measurement of the percent of the space of a particle occupied by micropores (pore diameter $< 2 \text{ \AA}$), mesopores (pore diameter $> 20 \text{ \AA}$ and $< 500 \text{ \AA}$), and macropores (pore diameter $> 500 \text{ \AA}$). A molecule cannot penetrate into a pore smaller than a given minimum diameter (depending upon the size of the molecule).

2.4.3.2 pH of humic acid solution

Value of pH of humic acid solution is an important factor in the adsorption of certain humic acid onto the adsorbent because the carboxyl, COOH, groups start to dissociate their protons at pH 3.0 and the humic molecule becomes negatively charged. At pH < 3.0 , the charge is very small, or even zero. At pH 9.0, the phenolic-OH groups also dissociate their protons, and the humic molecule attains a high negative charge.

2.4.3.3 Temperature of humic acid solution

Increasing the temperature must increase the mobility of the humic acid from the bulk solution towards the adsorbent surface. Furthermore, increasing temperature may produce a swelling effect within the internal structure of the adsorbent enabling large humic acid to penetrate further.

2.4.3.4 Agitation

The increase in the rate of HA removal by agitation may be attributed to the decrease in the diffusion layer thickness surrounding the adsorbent particles then humic acid molecules can though pass the film to penetrate on the adsorbent.

2.4.4 Adsorption isotherm

Adsorption isotherm is an equilibrium distribution of a chemical between the adsorbate concentration (mass per volume) and its adsorbed concentration at surface (mass adsorbate per mass adsorbent) applied at the constant temperature.

Adsorption isotherm can be classified into four types (L, S, C and H) as shown in Figure 2.9. A L-type isotherm describes the high affinity of adsorption between adsorbate and adsorbent at low concentration but the adsorption decrease as the concentration is further increase. The S-type describes the low affinity adsorption at low concentration, because of adsorbate-adsorbate interaction on adsorbent in the ligand saturation is reached, the adsorption precedes which increases affinity adsorption at higher concentration. The C-type describes a partition mechanism without any specific bonding between the adsorbate and adsorbate. The interaction is generally a hydrophobic adsorbate partition with hydrophobic adsorbent. The H-type describes a strong adsorbate-adsorbate interaction which occurs by chemisorption interactions. This type is extreme case of the L-type.

There are many types of adsorption isotherm depending on the composition of adsorbent and the properties of adsorbate.

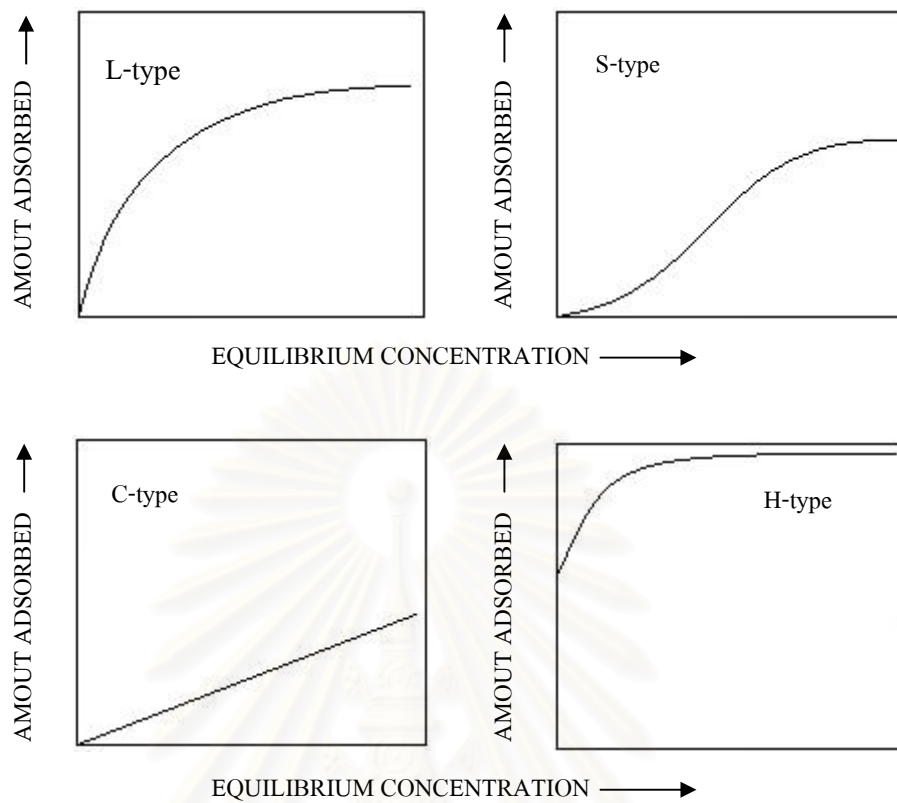


Figure 2.9 Classification of type of adsorption isotherm

The very common adsorption isotherms used in the adsorption processes are the Freundlich isotherm, and the Langmuir isotherm.

(a) Freundlich adsorption isotherm

The Freundlich is the mathematical approach for the experimental data of adjustable parameter to account for the variation in adsorption heat on an energetic heterogeneity of surface with the concentration of adsorbate. The relationship is describes by Equation 2.10.

$$Q_e = K_f C_e^{1/n} \quad (2.10)$$

where Q_e = the quantity of HA adsorbed per unit weight of adsorbent (mg/g)

K_f = the Freundlich affinity parameter for a hetero-disperse system (L/g)

C_e = the equilibrium concentration of HA in solution (mg/L)

n = the adsorptive intensity related to the magnitude of the adsorption driving force and to the distribution of the energy site on the adsorbent

The Freundlich isotherm lies on the assumption that there are multiple types of adsorption sites acting in parallel and there are interact between adsorbate molecules. The difference adsorption free energy and total site abundance are display in each site type. The exponent is an indicative of the diversity of free energies. When $1/n = 1$, the isotherm is linear and free energy is constant over the concentration range; when $1/n < 1$, the isotherm can be deduce the weaker adsorption and weaker free energies; when $1/n > 1$, the isotherm can be deduce that more adsorbates are adsorbed in which the free energies for further adsorptions enhanced. In summary, higher $1/n$ means higher adsorption. The Freundlich equation can be linearized as shown in Equation 2.11.

$$\log Q_e = \log K_f + 1/n \log C_e \quad (2.11)$$

(b) Langmuir adsorption isotherm

Langmuir isotherm is based on the theoretical principle that the active site on the adsorption process is limited. The assumption concepts of this isotherm are the adsorption process is mono layer (each molecule occupies one sorption site) and the affinity of each site for adsorbate is the same with on interaction between adsorbate molecules. The expression of this isotherm can be described by Equation 2.12.

$$C_e/Q_e = C_e/Q_0 + K_L/Q_0 \quad (2.12)$$

where Q_e = the quantity of HA adsorbed per unit weight of adsorbent (mg/g)

C_e = the equilibrium concentration of HA in solution (mg/L)

Q_0 = the monolayer adsorption capacity (mg/g)

K_L = the constant related to the free energy of adsorption

2.5 Literature reviews; Removal of HA from water

Removal of HA from water treatment has attracted much of environmental and healthy considerations. Various methods have been studied for enhancing HA removal from natural water, including chemical precipitation, membrane filtration, ion exchange and adsorption.

Adsorption is one of the efficient methods in HA removal. In the past years, several adsorbents have been studied for HA adsorption including:

- Activated carbon prepared from biomass material [8]

Daifullah et al. studied the activated carbon prepared from rice husk impregnated with H_3PO_4 for the removal of HA. The amount uptake was found to be a direct function of the amount of H_3PO_4 at 500°C . It appears that the adsorption of HA will occur in the secondary micropores and mesopores which are dependent on the amount of phosphoric acid introduced into the raw material. It was found that the uptake of HA increases in the presence of Ca^{2+} ions, the adsorption process is endothermic and the reversibility of the process is incomplete due to the desorption needs large energy barrier to be overcome. The electrostatic attraction and surface complex formation are responsible for the adsorption of HA on the carbon surface.

- Metal-modified silica [3]

Moriguchi et al. studied the adsorption of humic substances by metal-modified silica. The result showed that $\text{SiO}_2\text{-Fe}$ is eventually the most useful adsorbent for removing humic substances in water. Under the present adsorption condition, namely, using 2 g/L of the silica adsorbent in 7.6 mL aqueous solutions of the humic substances, 93-97% of HA and 80-86% of FA can be removed in water. A statistics report shows that the mean concentration of humic substances in rivers and lakes is estimated at 0.5-4.0 mgC/L, corresponding to approximately 1.0-8.0 mg/L. Thereby, $\text{SiO}_2\text{-Fe}$ may be applied to an adsorbent as an alternative to charcoal, equipped in water purification plant, and the used $\text{SiO}_2\text{-Fe}$ may be further reused as a fertilizer since humic substances have plant-growing ability and silica strengthens plant parts.

- Pillared bentonite (PB) [70]

Peng et al. studied the adsorption of HA onto pillared bentonite (PB). The experimental data showed that the aluminum polycation PB was successfully prepared and is reported to be effective adsorbent for removal of HA from water. The specific areas and basal spacing reaches $111.3 \text{ m}^2/\text{g}$ and 1.98 nm , respectively. It is effective for the removal of HA with a high adsorption capacity of 537 mg/g , and adsorption is favored under acid conditions. Adsorption is dependent on ionic strength and dissolved NaCl enhanced adsorption. Over 97% removal was observed under natural pH conditions from HA solutions containing 10 mg/L Ca^{2+} or Mg^{2+} , which suggests that pillared bentonite can be an effective adsorbent for the removal of HA for drinking water purification.

- Irradiation-crosslinked carboxymethylchitosan [71]

Zhao et al. studied the new type of crosslinked CM-chitosan synthesized by irradiation technique any additives, proved to be solution in acid, basic media and some organic solvents. The crosslinked samples were found to possess positive zeta potential below pH 6, mainly due to the protonation of the amino groups. The studies of adsorption demonstrated that crosslinked CM-chitosan can be used as an adsorbent for the removal of HA under acidic pH condition ($\text{pH} < 6$), and pH 3.5 was found to be optimum pH. The amino groups of crosslinked CM-chitosan in a protonated state, which can form the surface complex with HA, were found to play the major role in the adsorption process. The adsorption kinetics was mainly affected by transport-limited mechanism. This study clearly confirms that the irradiation crosslinked CM-chitosan has a potential in applications of separation and concentration of HA.

- Zeolitic truffs [72]

Capasso et al. studied the adsorption of HA by phillipsite- and chabazite-rich Neapolitan Yellow Tuff (NYT) and a clinoptilolite-rich truff (CLT), both in the native and in Ca-enriched forms. Experimental data showed that Ca-enriched NYT is an effective adsorbent for removing HA from water. Its adsorption capacity is higher than that of CLT. HA adsorption by Ca-enriched NYT readily attained a pseudo steady-state, after which the truff/HA-solution system evolved in a

few months to a final equilibrium state characterized by a much higher adsorption capacity. Desorption experiments at high pH levels resulted in a HA recovery > 80%.

- Goethite [73]

Weng et al. studied the adsorption of HA onto goethite. In this paper, the LCD (ligand charge distribution) model is applied to describe the adsorption of HA. The model considers both electrostatic interactions and chemical binding between HA and goethite. The large size of HA particles limits their close access to the surface. Part of the adsorbed HA particle is located in the compact part at the goethite surface and the rest in the less structured diffuse double layer. The model can describe the effects of pH, ionic strength, and loading on the adsorption. Compared to fulvic acids, the adsorption of HA is stronger and more pH- and ionic-strength-dependent. The stronger pH dependency in HA adsorption is related to the larger number of protons that are coadsorbed with HA due to the higher charge carried by a HA particle than by a FA particle. The positive ionic-strength dependency of HA adsorption can be explained by the conformational charge of HA particles with ionic strength. At a higher ionic strength, the decrease of the particle size favors closer contact between the particles and the surface, leading to stronger competition with electrolyte ions for surface charge neutralization and therefore leading to more adsorption.

Previous literatures indicated that the removal of HA by rice husk ash has not been discussed before and no literature data are available in this respect. However, previous adsorbents and chemicals are expensive. In this study, using low-cost adsorbent for adsorption has been much interested.

CHAPTER III

EXPERIMENTAL SECTION

3.1 Apparatus

3.1.1 UV-Vis spectrophotometer

A UV-Vis spectrophotometer model HP 8453 (Hewlett Packard) was used for the determination of humic acid concentration in aqueous solution at a wavelength of 254 nm.

3.1.2 pH meter

A pH meter model pH 211 (Hanna instruments) was used for pH measurements.

3.1.3 Manifold

A column method was performed using a VisiprepTM Vacuum Manifold (Supelco) connected to a vacuum pump.

3.1.4 Centrifuge

A centrifuge Centaur2 (Sanyo[®]) was used at 3500 rpm for 5 min to separate adsorbent from HA solution in batch method.

3.1.5 Muffle furnace

A muffle furnace (Nabertherm) was used for heating rice husk.

3.1.6 Elemental analyzer

An elemental analyzer (Perkin Elmer PE2400 SeriesII) was used for the carbon, hydrogen, and nitrogen (CHN) analysis.

3.1.7 X-ray diffractometer

X-ray diffraction (XRD) analysis was carried out using an X-ray diffractometer (Rikaku).

3.1.8 Scanning electron microscope

Scanning electron microscope (SEM) analysis of the rice husk ash was done using a scanning electron microscope (JEOL Model JSM-5410LV).

3.1.9 Surface area analyzer

Textural characteristics, such as the specific surface area, pore volume, and pore diameter of the rice husk ash were determined by nitrogen adsorption using a surface area analyzer (Quantachrome, Autosorb-1).

3.1.10 FTIR spectrometer

A FTIR spectrometer (Nicolet Impact 410) was employed to determine the presence of functional groups in the rice husk ash at room temperature.

3.2 Chemicals

All chemicals were of standard analytical grade listed in Table 3.1. They were used without further purification unless otherwise noted.

Table 3.1 List of chemicals used in the experiments

Chemicals	Suppliers
3-aminopropyltriethoxysilane	Merck
Calcium hydride	Fluka
Ethanol	Merck
Dichloromethane	Merck
Humic acid sodium salt (87.6%)	Aldrich
Hydrochloric acid 37%	Merck
Potassium bromide	Fluka
Sodium hydroxide	Merck
Toluene	Fisher Scientific

3.3 Humic acid purification

HA in its sodium salt was purchased from Aldrich. To purify the sample, 10 g of the HA was added to 1 L of NaOH solution with pH 11.0, stirred overnight and centrifuged to remove undissolved matter. To precipitate the HA fraction, the supernatant solution was brought to pH 2.0 with 1 M aqueous HCl, stirred for 24 h and centrifuged. The precipitate was rinsed with 0.01 M HCl several times to bring the HA in its proton form and to remove soluble fractions and inorganic salts. The HA was dried at 110 °C for 24 h for further use.

3.4 Preparation of humic acid solution

Stock standard solution of HA was prepared by 0.1 g of purified HA added to 1 L of 0.1 M NaOH solution, the mixture was stirred for 48 h and then filtered through filter papers (Whatman no.1). Working standard solutions were prepared by dilution of 100 mg/L HA stock standard solution to the required concentrations.

All working standard solutions were freshly prepared. The pH of solution was adjusted with HCl and NaOH solutions. All solutions were prepared by de-ionized water.

3.5 Preparation of rice husk ash

The rice husks were washed with de-ionized water to remove dirt and other contaminants and then dried in an oven at about 110 °C for 24 h.

3.5.1 Regular burning

For the regular burning, the washed and dried rice husks (40 g) were burned in air. After burning, the burned rice husks were crushed to obtain an approximate diameter size of < 2 mm. The prepared rice husk ash represents the rice husk ash from the process of rice manufacture.

3.5.2 Thermal treatment

The washed and dried rice husks were prepared by immersing rice husks in 1 N HCl and 1 N NaOH solutions for 4 h, compared with de-ionized water, at a ratio of 40 g husk/L. The husks were washed repeatedly with de-ionized water and then dried in an air oven at 110 °C. Samples of rice husks were converted into an adsorbent- rice husk ash (RHA) by heat-treating rice husks in ceramic crucibles at 350 °C and 700 °C for 6 h. The heated rice husks were crushed to obtain an approximate diameter size of < 2 mm. The preparation conditions and the notation of the samples were described in Table 3.2.

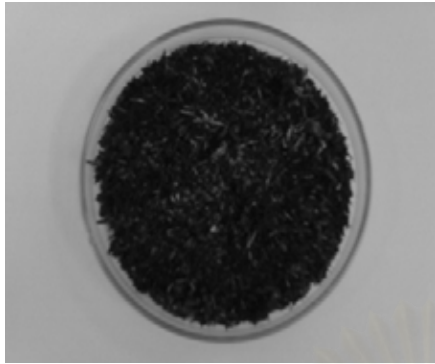
The prepared RHA were dried at 110 °C for 24 h before use and were stored in a desiccator.

Table 3.2 Preparation conditions of rice husk ash

Sample name	<i>Condition</i>	
	Treatment	Temperature (°C)
Ash	-	-
W-350	De-ionized water	350
A-350	HCl	350
B-350	NaOH	350
W-700	De-ionized water	700
A-700	HCl	700
B-700	NaOH	700

The pictures of the prepared RHA were illustrated in Figure 3.1.

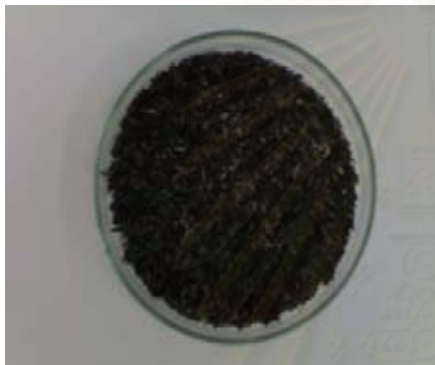
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Ash



W-350



A-350



B-350



W-700



A-700

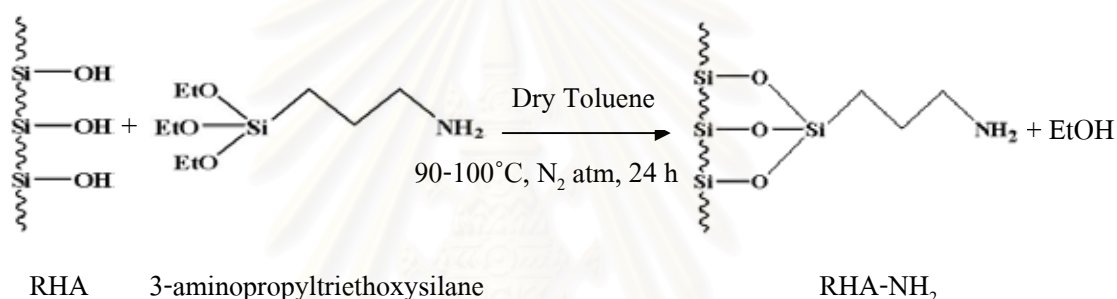


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Figure 3.1 Pictures of rice husk ash

Based on literature data [74], 25 g of RHA was mixed with 200 mL of dried toluene. The mixture was then refluxed under nitrogen atmosphere for 2 h and then 10 mL of 3-aminopropyltriethoxysilane (APTS) was added by a dropper, the mixture was refluxed again for 24 h. The solid was filtered, rinsed with ethanol and dichloromethane for 3 times and then dried at the room temperature. The modified RHA are called “RHA-NH₂”. The reaction is depicted in Scheme 3.1.



Scheme 3.1 Synthetic route for the modification of RHA with 3-aminopropyltriethoxysilane

3.7 Characterization of adsorbents

Physical and chemical characterizations of RHA were performed using standard procedures. Proximate analysis was carried out using a standard procedure. Carbon, hydrogen and nitrogen (CHN) analysis of RHA was done using an elemental analyzer. X-ray diffraction (XRD) analysis was carried out to identify the component of RHA. Scanning electron microscopic (SEM) analysis of RHA was carried out by using a scanning electron microscope.

Textural characteristics were determined by nitrogen adsorption using Brunauer-Emmett-Teller (BET) method. FTIR spectrometer was performed to determine the presence of functional groups in RHA.

The pH of adsorbent was measured as follows: 0.05 g of various RHA samples was mixed with 10 mL of de-ionized water and shaken for 2 h. After filtration, the pH of solution was determined by a pH meter.

3.8 Adsorption study

The adsorption studies were divided into two parts: batch and column methods.

3.8.1 Batch method

To study the optimum condition of HA adsorption for RHA and RHA-NH₂. Several factors affecting the adsorption process, i.e., contact time, pH of solution and initial concentration, were studied. The adsorbed amount of HA per weight unit of adsorbent at time t , $q(t)$ (mg/g), was calculated from the mass balance Equation 3.1.

$$q(t) = (C_0 - C_t)V / m \quad (3.1)$$

where C_0 = the initial HA concentration (mg/L)

C_t = the HA concentration at time t (mg/L)

V = the volume of the HA solution (mL)

m = the mass of the adsorbent (g)

3.8.1.1 Contact time

The HA solution was prepared by dilution of 100 mg/L HA stock solution in de-ionized water and final concentration was 50 mg/L (pH 6.0). In all case, an aliquot of 10 mL of HA solution was contacted with 50 mg adsorbents in stoppered glass bottles. The experiments were conducted in a shaker for a different contact time ranging from 3 to 120 min. The samples were taken out for centrifugation separation and filtered throughout 0.45 μ m filter membrane. A UV-Vis spectrophotometer was used for the determination of HA concentration at 254 nm.

3.8.1.2 pH of solution

The HA solutions were prepared by dilution of 100 mg/L HA stock solution in de-ionized water and final concentration was 50 mg/L. The effect of pH on the adsorption was studied by adjusting the pH of solutions in the range of 3.0 to 11.0. In all case, an aliquot of 10 mL of HA solution was contacted with 50 mg adsorbents in stoppered glass bottles. The experiments were conducted in a shaker for 60 min. The samples were taken out for centrifugation separation and filtered throughout 0.45 μm filter membrane. A UV-Vis spectrophotometer was used for the determination of HA concentration at 254 nm.

3.8.1.3 Initial concentration

The HA solutions were prepared by dilution of 100 mg/L HA stock solution in de-ionized water and final concentrations were varied between 5 to 50 mg/L. In these experiments, an aliquot of 10 mL of HA solution was contacted with 50 mg adsorbents in stoppered glass bottles. The experiments were conducted in a shaker for 60 min. The samples were taken out for centrifugation separation and filtered throughout 0.45 μm filter membrane. A UV-Vis spectrophotometer was used for the determination of HA concentration at 254 nm.

3.8.1.4 Adsorption isotherm

For the adsorption isotherm study, working solutions were prepared by dilution of 100 mg/L HA stock solution in de-ionized water and final concentrations were varied from 5 to 50 mg/L under optimum pH 6.0. In all case, an aliquots of 10 mL of HA solution were added to 50 mg of adsorbents in test tubes. The experiments were stirred for 60 min, and the temperature was controlled at 298 ± 1 K. The samples were taken out for centrifugation separation and filtered throughout 0.45 μm filter membrane. A UV-Vis spectrophotometer was used for the determination of HA concentration at 254 nm.

3.8.2 Column method

A disposable syringe, 1 cm in diameter and 10 cm in height, was used as a column. Each column contained 0.5 g of adsorbent. The column was loaded with 200-400 mL of 20 mg/L of HA solution (pH 6.0) at a flow rate of 1.5 mL/min by vacuum manifold. The concentration of HA in the effluent was determined by UV-Vis spectrophotometer at 254 nm.

3.9 Application for real sample

Surface water (from a pond in Chulalongkorn University) 1,000 mL was collected and filtered through 0.45 μm filter membrane. The HA solution was prepared by dilution of 100 mg/L HA stock solution in filtered surface water and the final concentration was 20 mg/L (pH 6.0).

A disposable syringe, 1 cm in diameter and 10 cm in height, was used as a column. Each column contained 0.5 g of adsorbent. The column was loaded with 200-400 mL of HA solution at a flow rate of 1.5 mL/min by vacuum manifold. The concentration of HA in the effluent was determined by UV-Vis spectrophotometer at 254 nm.

3.10 Comparison of adsorption efficiency with commercial activated carbon

Each adsorption experiment was conducted in stoppered glass bottles. Two types of commercial activated carbons such as granular activated carbon (GAC; Mazuma) and powder activated carbon (PAC; Merck) were used in this investigation. The volume was 10 mL of 50 mg/L HA solution containing 50 mg of the adsorbents. The experiments were conducted in a shaker for 60 min. The samples were taken out for centrifugation separation and filtered through 0.45 μm filter membrane. The concentration of HA was analyzed using UV-Vis spectrophotometer at 254 nm.

3.11 Analytical techniques

This section describes analytical techniques. The UV-Vis spectrophotometer was used for determining the residual HA in solution. The adsorbents were analyzed by elemental analysis (EA), scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and surface area and pore volume analysis (BET). Analytical procedures are described below but analytical results were shown in Chapter IV.

3.11.1 Determination of humic acid concentration

Amount of humic acids adsorbed is usually defined in terms of difference between the initial and final humic acids concentrations. UV-Vis spectrophotometry is the most commonly used technique for quantitative determination of humic acids concentration. Usually the Beer-Lambert law is employed to determine the concentration of humic acid in solution from a measurement of absorbance at wavelength of maximum absorption humic acids.

3.11.2 The elemental analysis of adsorbents

Elemental analysis is a procedure for analysis of some material samples (e.g., soil, waste or drinking water, minerals, chemical compounds) for its elemental composition. This process can be qualitative (determining what elements are present), and it can be quantitative (determining how much of each are present).

For synthetic chemists, elemental analysis or “EA” almost always refers to CHN analysis - the determination of the percentage weights of carbon, hydrogen, and nitrogen of a sample. This information is important to help determine the structure of an unknown compound, as well as to help prove the structure and purity of a synthesized compound.

The most common form of elemental analysis is accomplished by combustion analysis. In this technique, a sample is burned in an excess of oxygen, and various traps collect the combustion products - carbon dioxide, water, and nitric oxide. The weights of these combustion products can be used to calculate the composition of the unknown sample.

3.11.3 The surface structure of adsorbents

The scanning electron microscope (SEM) is a type of electron microscope capable of producing high-resolution images of a sample surface. Due to the manner in which the image is created, SEM images have a characteristic three-dimensional appearance and are useful for judging the surface structure of the sample.

In a typical SEM, electrons are emitted from a tungsten or lanthanum hexaboride (LaB₆) cathode and are accelerated towards an anode; alternatively, electrons can be emitted via field emission (FE). Tungsten is used because it has the highest melting point and lowest vapour pressure of all metals, thereby allowing it to be heated for electron emission. The electron beam, which typically has an energy ranging from a few hundred eV to 100 keV, is focused by one or two condenser lenses into a beam with a very fine focal spot sized 1 nm to 5 nm. The beam passes through pairs of scanning coils in the objective lens, which deflect the beam horizontally and vertically so that it scans in a raster fashion over a rectangular area of the sample surface. When the primary electron beam interacts with the sample, the electrons lose energy by repeated scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to around 5 μm into the surface. The size of the interaction volume depends on the beam accelerating voltage, the atomic number of the specimen and the specimen's density. The energy exchanges between the electron beam and the sample results in the emission of electrons and electromagnetic radiation which can be detected to produce an image.

3.11.4 The structure of adsorbents

X-rays are electromagnetic radiation of wavelength about 1 \AA (10⁻¹⁰ m), which is about the same size as an atom. They occur in that portion of the electromagnetic spectrum between gamma-rays and the ultraviolet. X-ray diffraction has been in use in two main areas, for the fingerprint characterization of crystalline materials and the determination of their structure. Each crystalline solid has its unique characteristic X-ray powder pattern which may be used as a "fingerprint" for its identification. Once the material has been identified, X-ray crystallography may be used to determine its structure, i.e. how the atoms pack together in the crystalline state

and what the inter-atomic distance and angle are etc. X-ray diffraction is one of the most important characterization tools used in solid state chemistry and materials science.

3.11.5 The study of functional groups on adsorbents

Fourier transform infrared spectroscopy (FTIR) is most useful for identifying chemicals that are either organic or inorganic. It can be utilized to quantitate some components of an unknown mixture. It can be applied to the analysis of solids, liquids, and gasses. The term Fourier transform infrared spectroscopy (FTIR) refers to a fairly recent development in the manner in which the data is collected and converted from an interference pattern to a spectrum. FTIR instruments are computerized which makes them faster and more sensitive than the older dispersive instruments. FTIR can be used to identify chemicals from spills, paints, polymers, coatings, drugs, and contaminants. FTIR is perhaps the most powerful tool for identifying types of chemical bonds (functional groups).

Molecular bonds vibrate at various frequencies depending on the elements and the type of bonds. For any given bond, there are several specific frequencies at which it can vibrate. According to quantum mechanics, these frequencies correspond to the ground state (lowest frequency) and several excited states (higher frequencies). One way to cause the frequency of a molecular vibration to increase is to excite the bond by having it absorb light energy.

The samples for FTIR can be prepared by milled solid samples with potassium bromide (KBr) at ratio 1:100 to form a very fine powder. This powder is then compressed into a thin pellet which can be analyzed. KBr is also transparent in the IR.

3.11.6 The surface area and pore volume of adsorbents

A surface area analyzer was used to determine surface area, pore volume, and pore size distribution of adsorbent. The instrument detects the volume of adsorbed nitrogen gas on surface at various relative pressures. There are two operating steps, degassing step and analysis step.

Firstly, the adsorbent was heated and placed under vacuum to remove moisture and other contaminants. Temperature of degassing was carried out at 150 °C and vacuum until pressure dropped to 10 mmHg. After that, the sample was weighed and then the degassed sample was transfer from the degas port to the analysis port.

At the analysis port, the sample was analyzed at vacuum pressure of 15 mmHg and liquid nitrogen was used as a coolant. The nitrogen gas was used as analysis gas. The volume of adsorbed nitrogen on sample will relate with relative pressure (P/P_0). The volumes of adsorbed nitrogen gas and relative pressure were plotted the graph. The Y-intercept and slope of the graph was calculated BET surface area of sample.



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CHAPTER IV

RESULTS AND DISCUSSION

In this chapter, the results are divided into five parts; (i) the preliminary study, (ii) the characterization of the adsorbents, (iii) the adsorption of HA using batch method, several factors affecting the adsorption process, e.g., contact time, pH, and initial concentration were studied, (iv) the adsorption capacity of adsorbents in column method, and (v) the comparative efficiency of rice husk ash and commercial activated carbon to adsorb HA.

4.1 Preliminary study: effect of preparation mode

A series of the RHA were prepared from rice husk by heating at two different temperatures. The elemental composition of the RHA is given in Table 4.1. The result indicated that the color of the prepared RHA can be divided into three groups, black-brown, grey, and white. The heating of rice husk at different temperatures produced ashes containing different content of carbon. The RHA heated at 700 °C had low percentages of carbon. Nakbanpote *et al.* [18] have been reported that the carbon was lost when heated at ≥ 400 °C. This was also the primary reason for the large difference in carbon content between RHA (350 °C) and RHA (700 °C). The pH values of the slurry solution with different solid samples indicates that the acid-treated RHA exhibit weak acidity in the solution, the base-treated RHA exhibits slight basic characteristic in the solution and the pH appears neutral for the non-treated RHA. This is due to the chemicals used that can be incorporated inside the adsorbent.

In this study, the initial pH value at 6.0 of HA solution was selected due to the pH of water was almost in the range of 5.0-7.0 [2]. The seven different RHA were compared for the adsorption of HA. The result is illustrated in Figure 4.1. The preliminary test showed that the natural rice husk had no ability for adsorption of HA and the highest capacity was 1.97 mg/g by A-700. Table 4.1 illustrates the relationship between HA adsorption and carbon content. This suggests that carbon has no significance in its adsorptive capacity for HA. The best temperature was 700 °C which produced suitable property of RHA for HA adsorption. Compared with the

variation of solid slurry pH, it is seen there is no significant relationship. This can be seen that the chemical treatment in the preparation of RHA did not affect the HA adsorption. The adsorbent A-700 (hereafter called “RHA” for simplicity) is only used in further experimental runs because of the highest capacity. The aims were used for the surface modification experiment and to find out the effect of various parameters on its affinity towards the uptake of HA.

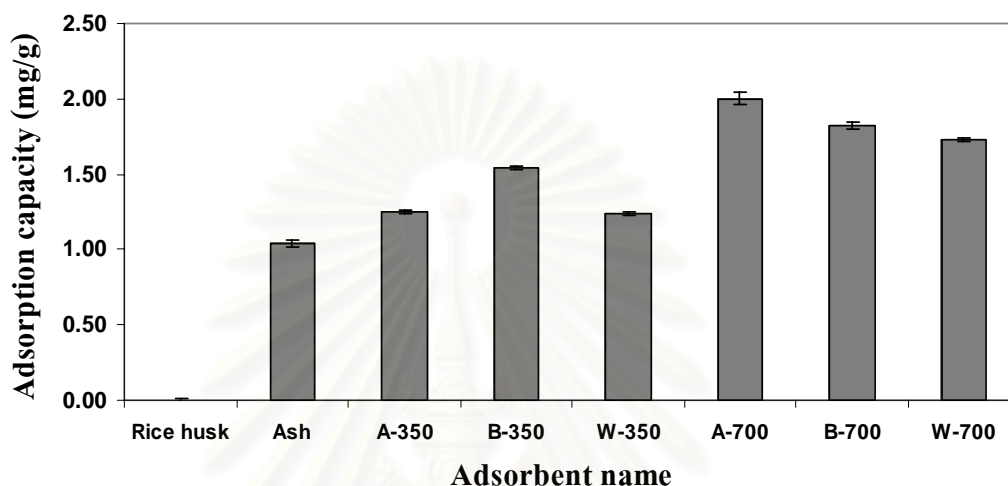


Figure 4.1 Adsorbability of HA onto rice husk and different RHA; HA concentration = 20 mg/L; volume = 10 mL and adsorbent dose = 50 mg, pH = 6.0 (n=3)

Table 4.1 Elemental composition and adsorbability of HA onto different RHA

Adsorbent name	Color	pH	Elemental composition (%)			Adsorption capacity (mg/g) ^{a,b}
			C	H	N	
Ash	Grey	7.87	10.34	0.60	n.d.	1.01±0.01
W-350	Black-brown	6.95	17.63	1.31	n.d.	1.21±0.04
A-350	Black-brown	6.44	83.22	0.73	n.d.	1.23±0.02
B-350	Black-brown	8.74	13.01	0.21	n.d.	1.52±0.02
W-700	Grey	7.55	0.17	n.d.	n.d.	1.71±0.01
A-700	White	6.28	0.13	0.11	n.d.	1.97±0.04
B-700	Grey	8.78	0.63	0.02	n.d.	1.79±0.02

^a HA concentration = 20 mg/L; volume = 10 mL and adsorbent dose = 50 mg, pH = 6.0.

^b Mean value ± SD (n = 3)

n.d. = not detectable

4.2 Characterization of adsorbents

The present study deals with the characterization of low-cost adsorbents for its various physical and chemical characteristics. The results are illustrated in Table 4.2.

Table 4.2 Physical and chemical characteristics of RHA and RHA-NH₂

Property	Adsorbent	
	RHA	RHA-NH ₂
Color	White	White
C, %	0.13	4.19
H, %	0.11	0.61
N, %	n.d.	0.93
pH	6.28	8.72
Average pore diameter, Å	56.93	175.80
Total pore volume, mL/g	0.2735	0.1006
BET surface area, m ² /g	192.13	22.88

n.d. = not detectable

4.2.1 pH of adsorbent

The pH of slurry solution with two adsorbents indicates that RHA surface was weak acidic, the higher pH of RHA-NH₂ was caused by the basic characteristic of amino group on the adsorbent surface.

4.2.2 Elemental analysis

The elemental analysis is very important technique to confirm the success of the modification of RHA surface with APTS and explained in term of the adsorption process. The elemental composition of the adsorbents is given in Table 4.2.

For the RHA, the elemental analysis showed 0.13% carbon, 0.11% hydrogen and nitrogen was undetectable. CHN analysis of the RHA-NH₂ showed 4.19% carbon, 0.61% hydrogen and 0.93% nitrogen, the increasing percentage of carbon and nitrogen was due to the APTS molecules on the RHA surface. It reveals the success of the surface modification by APTS.

4.2.3 SEM analysis

Textural characteristic was carried out by using a scanning electron microscope. The microscopic observation (Figure 4.2) shows its surface texture and porosity. SEM analysis of RHA reveals particles that are irregular shaped and very fine particle size to the order of millimeter or less and that there are pores of varying sizes within the particle. After reacting with APTS, the ash appears irregular shaped that are uniformly distributed, varying sizes of pore are observed within the particle. The surface modification did not cause significant morphological change (Figure 4.3). According to the result, the presence of various pore sizes in RHA could enhance adsorption capacity.

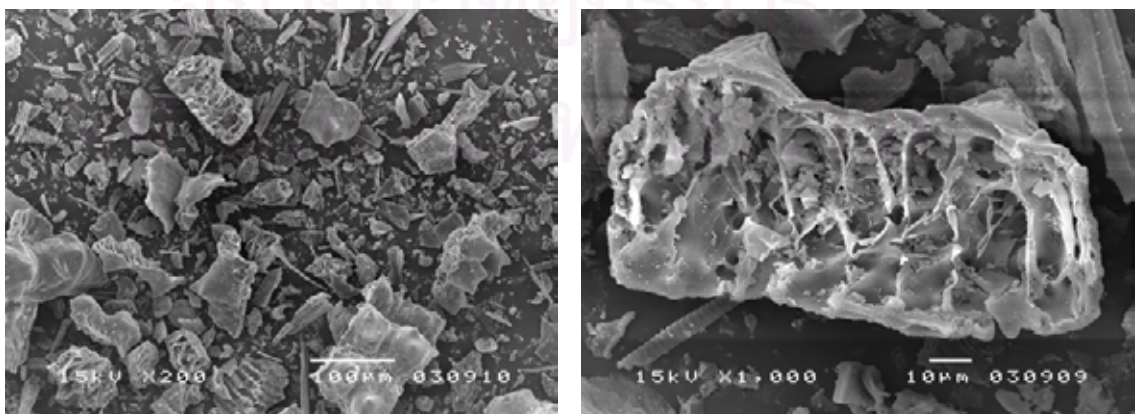


Figure 4.2 Scanning electron micrographs of RHA

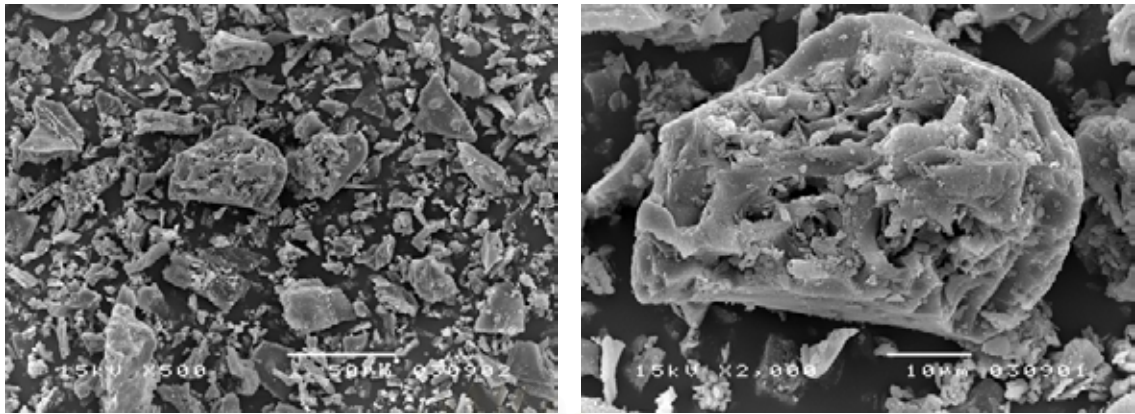


Figure 4.3 Scanning electron micrographs of RHA-NH₂

4.2.4 Surface area and pore volume analysis

Table 4.2 lists the data on surface area, pore volume, and pore diameter of the adsorbents. Based on these properties, it appears that the presence of high specific surface area on RHA will make them suitable for using as an adsorbent. Compared with the unmodified RHA, the RHA-NH₂ indicated smaller surface area and pore volume. The decrease of the surface area and pore volume reflects the occupation of small pore of the RHA by the APTS molecules. The increasing pore diameters of the RHA-NH₂ are due to the decrease of small pores in the similar reason.

4.2.5 FTIR spectroscopy

The chemical structure of adsorbent is of vital importance in understanding the adsorption process. The FTIR technique is an important tool to identify the characteristic functional groups, which are instrumental in adsorption of HA.

Figure 4.4a shows a broad band between 2800 and 3700 cm⁻¹ which indicates the presence of both OH groups and Si-OH group on the adsorbent surface. This stretching is due to both the silanol groups (Si-OH) and adsorbed water (peak at 3454 cm⁻¹) on the surface. The IR spectra indicated peaks about 1637 cm⁻¹ corresponding to -C=O and -C-OH group stretching. The silanol groups are in the form of silicon dioxide structure (-Si-O-Si-OH). This structure is similar to the silanol groups of silicic acid. The peak at 1100 cm⁻¹ is due to Si-O-Si and -C-O-H

stretching and –OH deformation. The peaks about 798 and 462 cm^{-1} indicate the presence of Si-H. According to the result, it appears that the presence of Si-OH in RHA will make them suitable for the modification reaction on the RHA surface with APTS as an aminopropyl silica.

The presence of aminopropyl groups is identified by the appearance of C-H groups [75]. The FTIR spectra of the modified RHA (Figure 4.4b) shows two additional small shoulders at 2924 and 2875 cm^{-1} assigned to the asymmetric and symmetric stretch vibrations of –CH₂ and –CH₃. According to the result, the silanol groups on the surface are the sites for incorporation of the aminopropyl groups and are consumed, i.e., the aminopropyl groups are chemically bonded on the surface of the RHA.

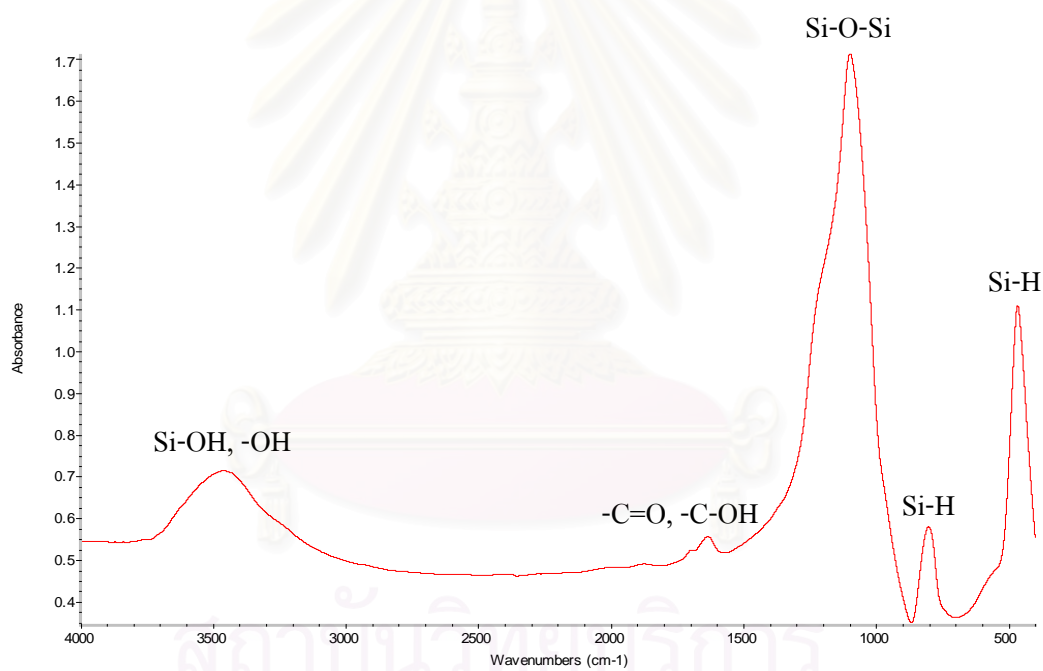


Figure 4.4 (a) Fourier transform infrared spectra of RHA

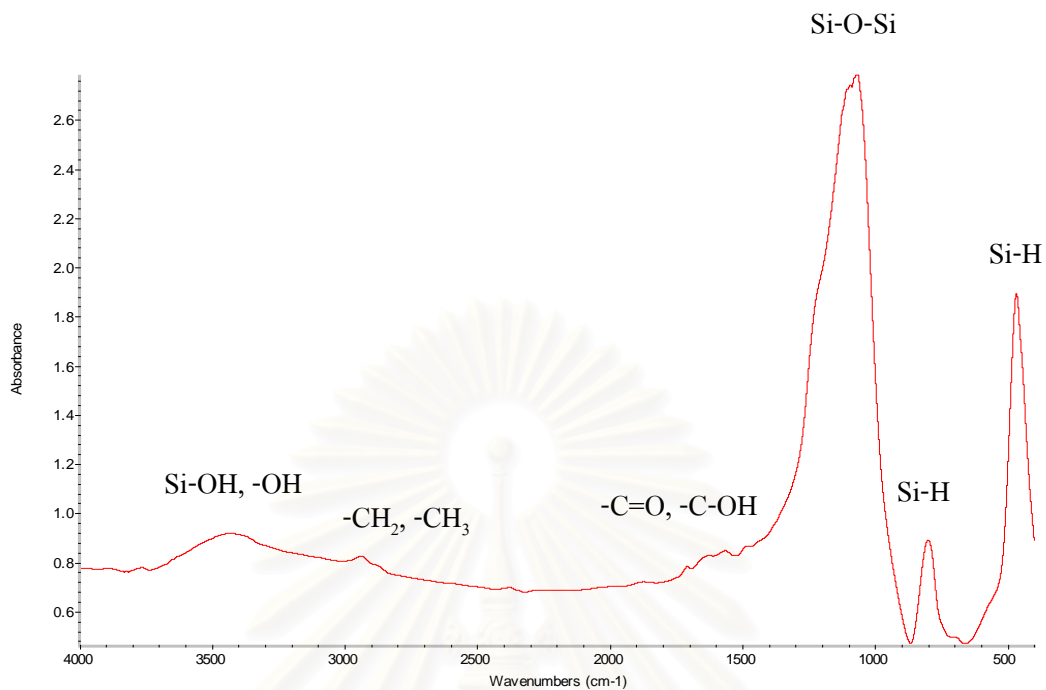


Figure 4.4 (b) Fourier transform infrared spectra of RHA-NH₂

4.2.6 X-ray diffraction

Burning temperature and time are important factors to define whether silica remains amorphous, as in RHA, or become crystalline. X-ray diffraction (XRD) analysis was carried out to identify the properties of adsorbents.

The X-ray diffraction patterns of RHA and RHA-NH₂ show a broad “hump” between 15 and 35° 2θ diffraction angle, whilst lacking any defined peaks (Figure 4.5). The result indicated that RHA and RHA-NH₂ were characteristic of amorphous substances, the heating RHA at 700 °C did not change the structure of silicon dioxide from an amorphous structure to a crystalline structure (observed at 2θ=22°), such as quartz, cristobalite or tridimite. Formation of amorphous silica (purity 99.6%) from rice husk is also reported by Yalcin and Sevinc [12], and Proctor [76].

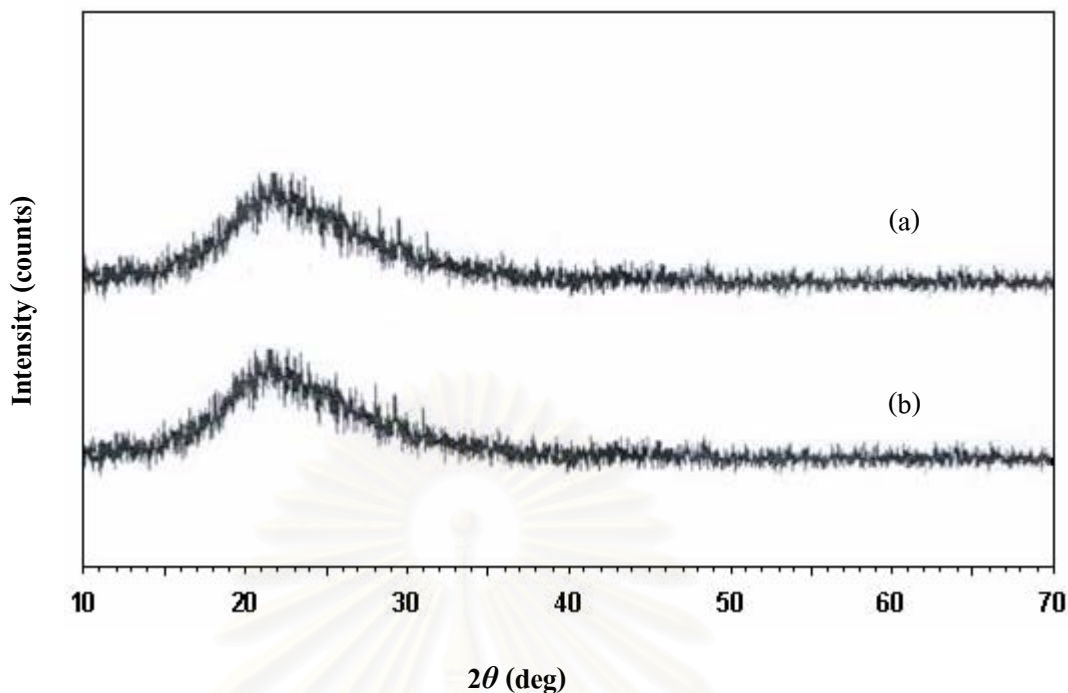


Figure 4.5 XRD patterns of (a) RHA and (b) RHA-NH₂

4.3 Adsorption study: batch method

4.3.1 Effect of contact time

The rate of loading of HA onto RHA and RHA-NH₂ were determined by agitating working standard solution with adsorbents at pH 6.0 with different contact times. Accordingly all the batch experiments were conducted with a contact time of 120 min under vigorous shaking conditions. The adsorption efficiencies in function of contact time were shown in Figure 4.6. The contact time required for reaching adsorption equilibrium was 60 and 30 min for the RHA and RHA-NH₂, respectively. The rate of HA adsorption onto RHA-NH₂ is sufficiently rapid. Therefore, it is suitable for the flow system.

The adsorption equilibrium time was due to the initial concentration which provided the necessary driving force to overcome the resistances to the mass transfer of HA between the aqueous and the solid phase, and the number of available surface sites for adsorption. During the initial stage of adsorption, a large number of vacant surface sites are available for

adsorption. After lapse of sometime, the remaining vacant sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid surface and the bulk phase. Besides, the HA are adsorbed into the mesopores that get almost saturated with HA during the initial stage of adsorption. Thereafter, the HA have to traverse and deeper into the pores encountering much larger resistance. This results in the slowing down of the adsorption during the later period of adsorption. According to these results, 60 min were chosen and used as the optimum condition for the further investigations.

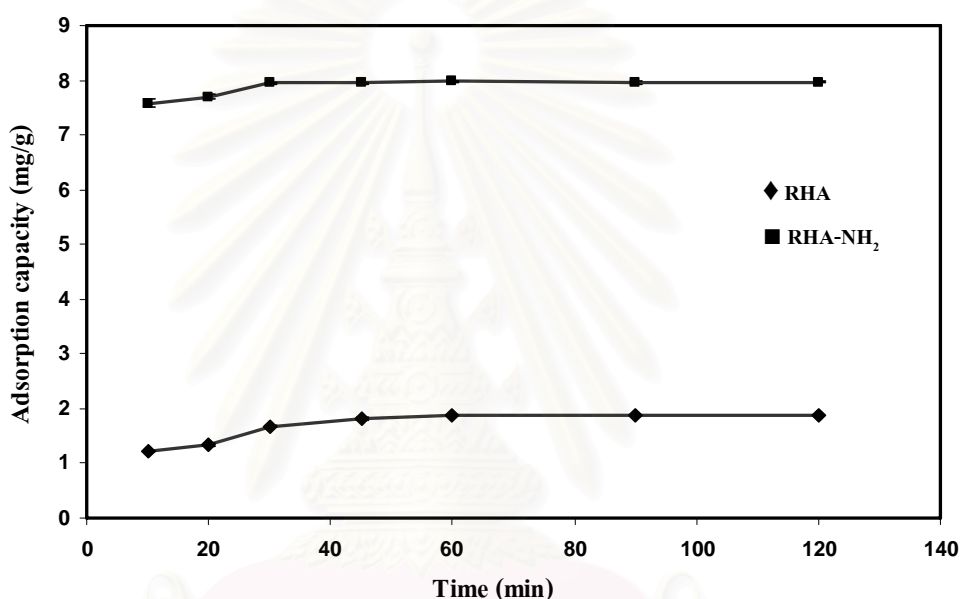


Figure 4.6 Effect of contact time of HA adsorption onto RHA and modified RHA

4.3.2 Effect of initial pH

The pH of the solution affects the surface charge of the adsorbents as well as the degree of ionization and speciation of different pollutants. Change in pH affects the adsorptive process through dissociation of functional groups on the active sites on the surface of the adsorbent. Adsorption of various anionic and cationic species on such adsorbents can be explained on the basis of the competitive adsorption of H^+ and OH^- ions with the adsorbates. It is a common observation that the surface adsorbs anions favorably at low pH due to presence of H^+ ions, whereas, the surface is active for the adsorption of cations at higher pH due to the deposition of OH^- ions.

Humic acids (HA), the major component of natural humic substances, contains both hydrophobic and hydrophilic moieties as well as many chemically functional groups such as carboxylic, phenolic, carbonyl and hydroxyl connected with the aliphatic or aromatic carbons to form macromolecule [7]. The negative charge of HA molecule in aqueous solution is a result of existence of carboxylic and phenolic groups in its structure and their deprotonation. Some researchers reported that the HA does not follow the macromolecule model, recently. According to the new theory, humic substances are collections of diverse, relatively low molecular mass components forming dynamic associations stabilized by hydrophobic interactions and hydrogen bonds [8]. In this study, we do not discuss the effect of macromolecule nature or small molecular nature on the adsorption process. However, from the both viewpoints, the pH of the solution appears very important in relation to the HA adsorption result due to pH changes on the molecular structure of HA.

As shown in Figure 4.7, the capacity of HA adsorption by RHA increases in general with decreasing initial pH, but there was hardly any adsorption over pH 5.0. The maximum adsorption of HA on the RHA was found at pH 3.0 due to lower solubility of HA. At the lower pH range (in acidic range) the surface of the RHA take up the H^+ ions from solution and hence, increasing the acidity of the adsorbent surface. On the other hand, HA are predominantly negatively charged due to abundance of carboxylic and phenolic groups and it has been note that the negative charged groups on adsorbed molecule (HA) will tend to associate with equivalent number of positive charged groups on the RHA surface, forming an “ion pair” and thus become unavailable for adsorption process. In this concern, the carboxylic group start to dissociate at pH value 3.0-7.0 and the phenolic group dissociate at relatively high pH value [3]. Such behavior causes a gradient decrease in the uptake of HA as pH increases due to the excess formation of ion-pairs. The remaining negatively charged groups on the HA are available and enhance the uptake of HA by electrostatic attraction between the opposite charges.

However, on increasing pH (in alkaline range), the percentage adsorption decreased substantially, due to, the RHA posses hydroxyl groups, which are fully deprotonated and negatively charged at $pH > 3.0$. Consequently, the uptake of HA would be reduced.

For the RHA-NH₂, the capacity of HA adsorption is found to increase in general with decreasing initial pH, but the adsorption capacity over pH 6.0 was constant. A sharp

decrease of HA adsorption was observed at pH between 3.5 and 6.0. The maximum adsorption of HA on the modified RHA was found at pH 3.0. Furthermore, the lower pH induced more protonated amino groups of the RHA-NH₂ for HA adsorption, and this can be explained why the RHA-NH₂ adsorbed HA efficiently in low pH condition. This result indicates that the HA adsorption mechanism onto the RHA-NH₂ can be suggested as the affinity between the negative functional groups (such as unprotonated carboxyl, phenolic groups) in HA with the positive functional groups (protonated amino group) onto the modified RHA (Figure 4.8). The aim of this research was to use the obtained experimental data for applying in the water treatment where the pH of water was almost in the range of 5.0-7.0 [2]. Therefore, we propose to use pH 6.0 for the further investigations.

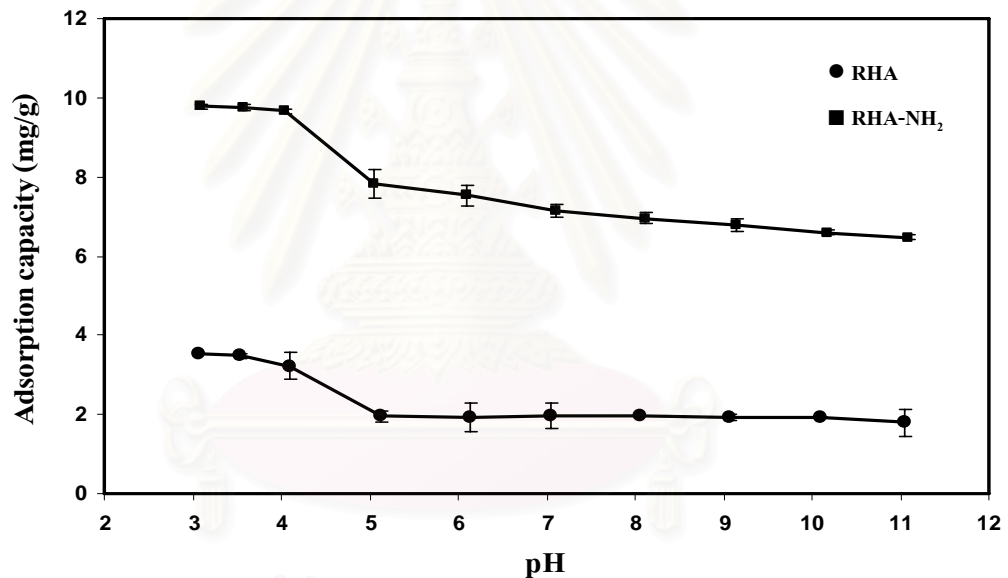


Figure 4.7 Effect of initial pH of HA adsorption onto RHA and RHA-NH₂

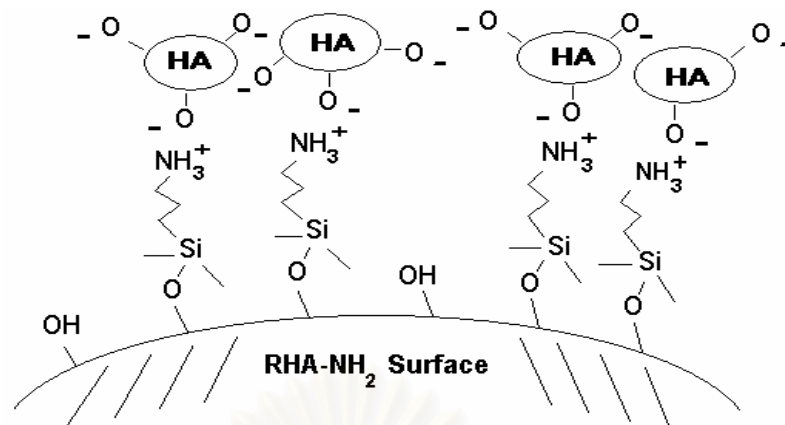


Figure 4.8 Schematic presentation of the interactions of HA with RHA-NH₂

Similar pH effect on HA adsorption have been reported during the adsorption of HA on other adsorbents such as activated carbon, chitosan and Pillared bentonite. In general, the humic acid consists of many polymeric components with major functional groups as carboxylic and phenolic. These groups can be ionized by increasing water pH to exhibit anionic characteristics. At high pH, the anionic species from HA will compete with OH⁻ to occupy the active sites of solid, resulting in the decrease of HA adsorption. At low pH, high adsorption of HA can be attributed to the charge reduction of weakly acidic humic acids as the pH was lowered.

A summary of the optimum pH values for the adsorption of HA varied in the different adsorbents is shown in Table 4.3.

Table 4.3 Values of optimum pH for humic acids adsorption varied in the different adsorbents

pH	Adsorbent	Reference
3.0	Activated carbon prepare from rice husk	[3]
3.1	Pillared bentonite	[70]
3.5	Irradiation-crosslinked carboxymethylchitosan	[71]
3.0-4.0	Goethite	[73]
3.0-4.0	Rice husk ash	Present work
3.0-4.0	Modified rice husk ash with 3-aminopropyltriethoxysilane	Present work

4.3.3 Effect of initial humic acid concentration

The effect of initial concentration on the extent of adsorption of HA onto RHA is shown in Figure 4.9. The capacity of HA adsorption increases with raising initial concentration of the solute up to 40 mg/L. Above this concentration and at the equilibrium, which was attained after 60 min of the contact between the solute and RHA, there was no further rise probably due to the limited active sites available to adsorb HA on the RHA surface. As anticipated, the large HA molecule could be adsorbed essentially on the external surface or in wider pores, and thus upon covering the surface a second layer was not favorable. The HA molecules would favorably go into solution instead of forming a second layer over the already adsorbed layer. The similar result has been observed for HA adsorption onto RHA-NH₂ also (Figure 4.10).

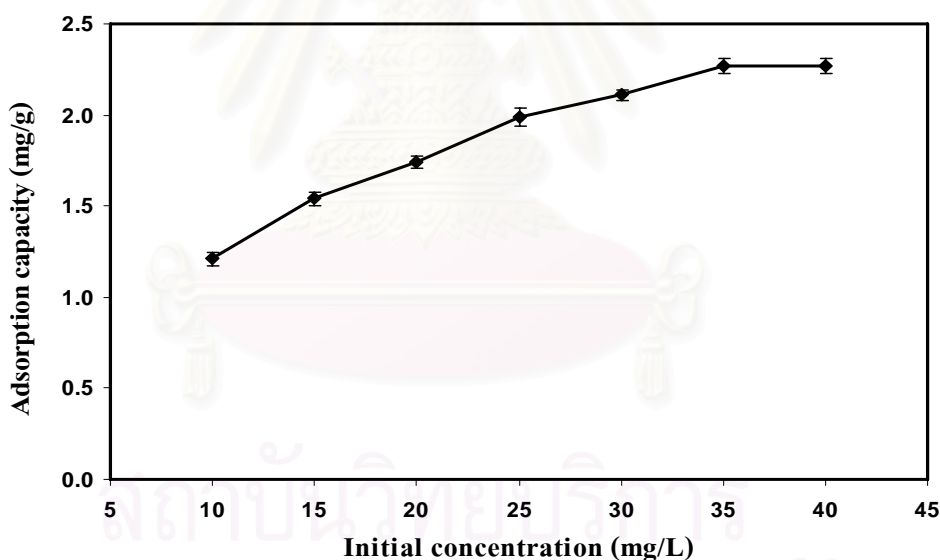


Figure 4.9 Effect of initial concentration on HA adsorption onto RHA

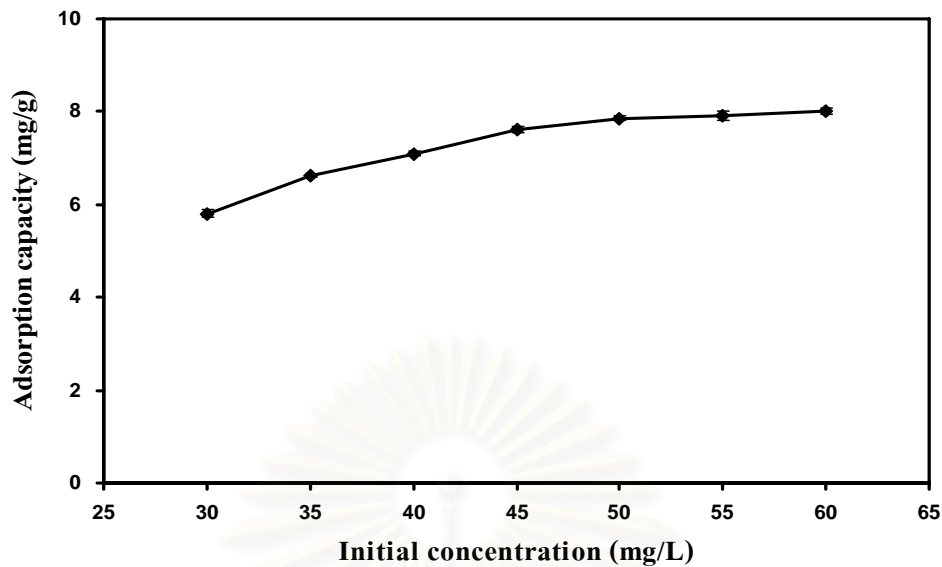


Figure 4.10 Effect of initial concentration on HA adsorption onto modified RHA

4.3.4 Adsorption isotherm

The relationship between the amount of a substance adsorbed at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm. The Langmuir and Freundlich isotherms are the equations most frequently used to represent data on adsorption from solution. The logarithmic form of the Langmuir isotherm and the linear form of the Freundlich isotherm equation are represented by the following equations:

$$\text{Langmuir equation : } C_e/Q_e = C_e/Q_0 + 1/bQ_0 \quad (4.1)$$

$$\text{Freundlich equation: } \log Q_e = \log K_F + 1/n \log C_e \quad (4.2)$$

where C_e = concentration of adsorbate at equilibrium (mg/L)

Q_0 = maximum solute concentration in the adsorbent

Q_e = amount of the adsorbed HA per unit weight of adsorbent at the final equilibrium HA concentration (mg/g)

b = a constant related to the energy of adsorption

K_F = Freundlich's constant related to the sorption capacity

n = Freundlich's constant related to the adsorption intensity of an adsorbent

Table 4.4 Langmuir and Freundlich model parameters for adsorption of HA

Adsorbent	Langmuir isotherm			Freundlich isotherm		
	Q_0 (mg/g)	b (L/mg)	R^2	K_F	$1/n$	R^2
RHA	2.72	0.177	0.9958	0.78	0.328	0.9897
RHA-NH ₂	8.20	1.882	0.9998	5.99	0.107	0.9480

- Langmuir isotherm

From Figure 4.11 and 4.12, which is a plot of C_e/Q_e vs C_e produces a straight line, which is an indication of the applicability of the Langmuir isotherm for the system under consideration. The adsorption of HA by RHA and RHA-NH₂ follows the Langmuir isotherm model. The Q_0 and b values presented in Table 4.4 are calculated from the slopes and intercepts of the plots. These values are used for comparison and correlation of the adsorptive properties of RHA and RHA-NH₂. Compared with Table 4.4, Q_e is smaller than Q_0 . This shows that the adsorption of HA by RHA and RHA-NH₂ is monolayer type adsorption in which the surface of RHA and RHA-NH₂ are not fully covered.

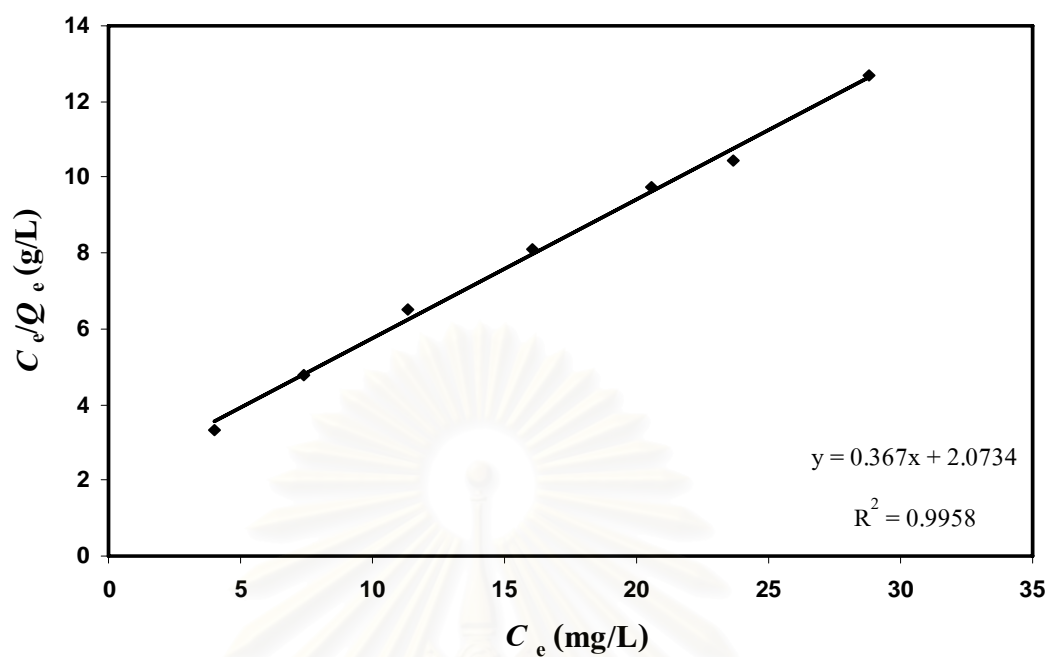


Figure 4.11 Linearized Langmuir plot for HA adsorption by RHA

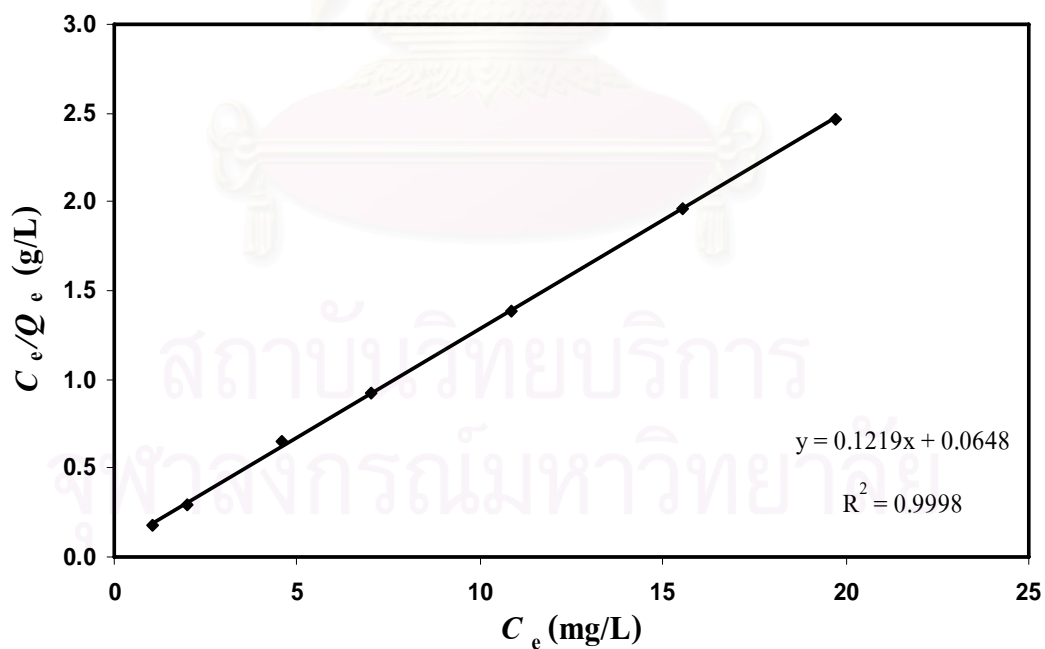


Figure 4.12 Linearized Langmuir plot for HA adsorption by RHA-NH₂

- Freundlich isotherm

From Figure 4.13 and 4.14, the $\log Q_e$ is plotted against $\log C_e$, a straight line with a slope $1/n$ and an intercept $\log K_F$ is obtained. This reflects the satisfaction of the Freundlich isotherm model for the adsorption of HA by RHA and RHA-NH₂. The intercept of the line, $\log K_F$, is roughly an indication of adsorption capacity and the slope, $1/n$, is an indication of adsorption intensity, The Freundlich parameters for the adsorption of HA are given in Table 4.4.

Plotting the experimental data using Equation 4.1 and 4.2 indicates that both models give good fits for the data for HA adsorption by RHA. The correlation coefficients show that, in general, the Langmuir model fitted the results slightly better than the Freundlich one. Moreover, the HA adsorption by RHA-NH₂ fits well the Langmuir model. It can only tell from the results that the adsorption of HA on RHA and RHA-NH₂ are monolayer or multilayer. The mechanism should be further investigated.

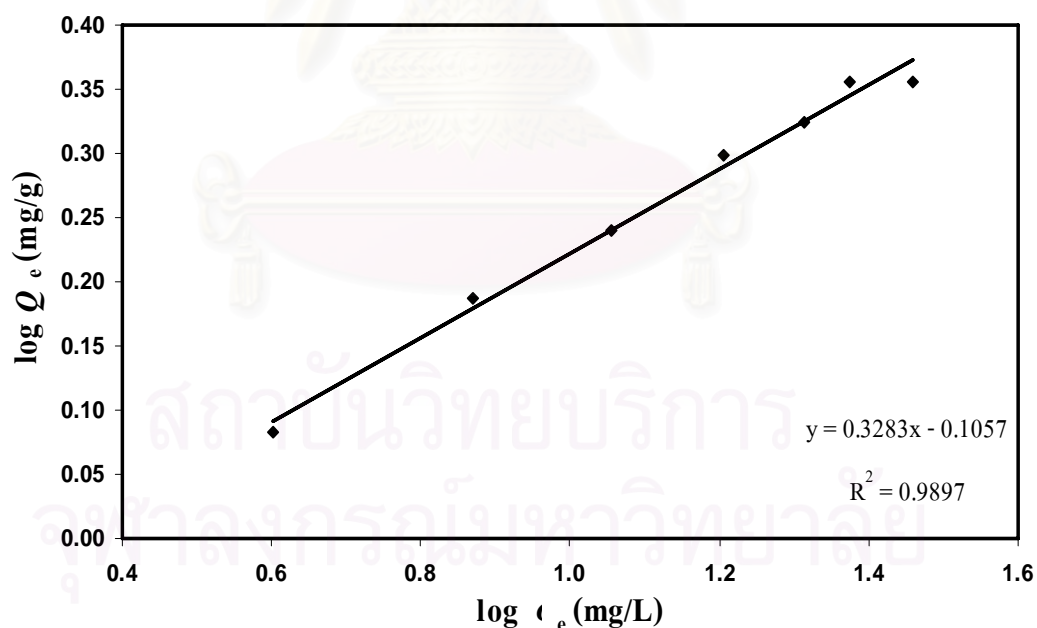


Figure 4.13 Linearized Freundlich plot for HA adsorption by RHA

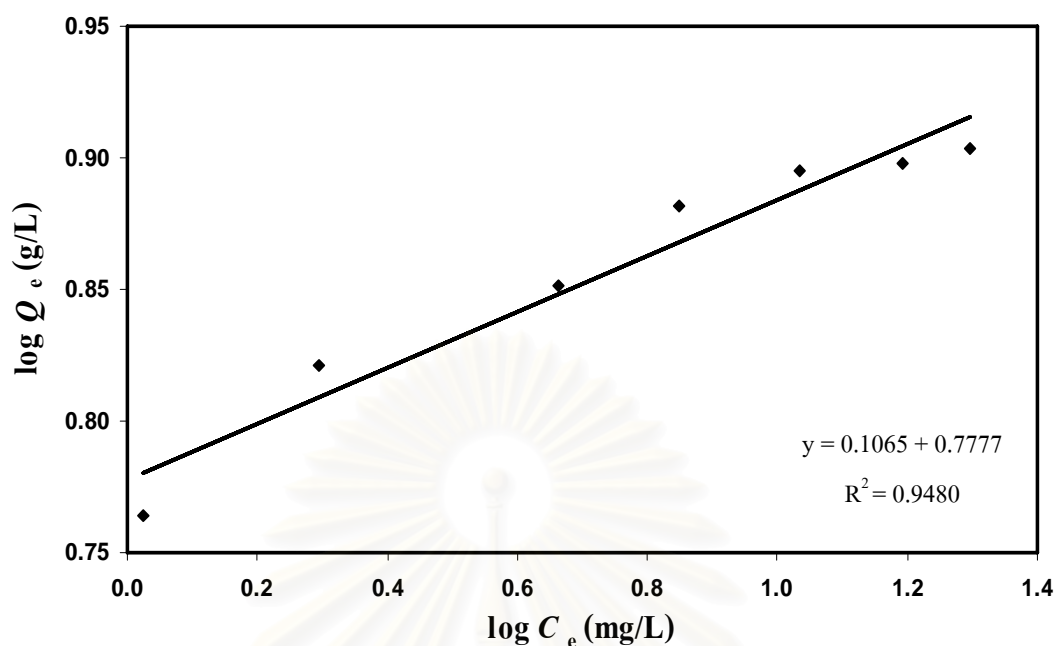


Figure 4.14 Linearized Freundlich plot for HA adsorption by RHA-NH₂

4.4 Adsorption study: column method

The breakthrough curves plotted between the concentrations of humic acids in the eluent against the volume of the solution are illustrated in Figure 4.15 and 4.16. The point on the curve at which some arbitrary amount of sample is detected at the outlet of adsorbent is the breakthrough volume (V_B). The results showed that V_B were 50 and 100 mL for RHA and RHA-NH₂, respectively.

A second point on the shape of the breakthrough curves is the maximum sample volume (V_M), corresponding to the volume at which the capacity of adsorbent is exceeded. It is found that V_M were 90 and 360 mL for RHA and RHA-NH₂, respectively.

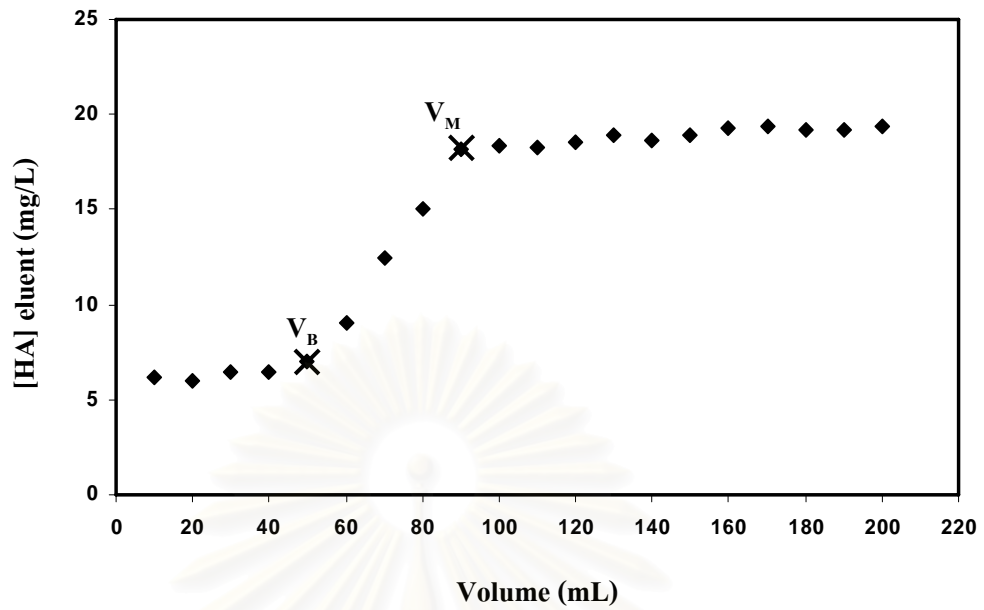


Figure 4.15 Breakthrough curve of RHA column (synthetic water); mass of adsorbent = 0.5 g, initial concentration = 20 mg/L, flow rate = 1.5 mL/min, and pH = 6.0.

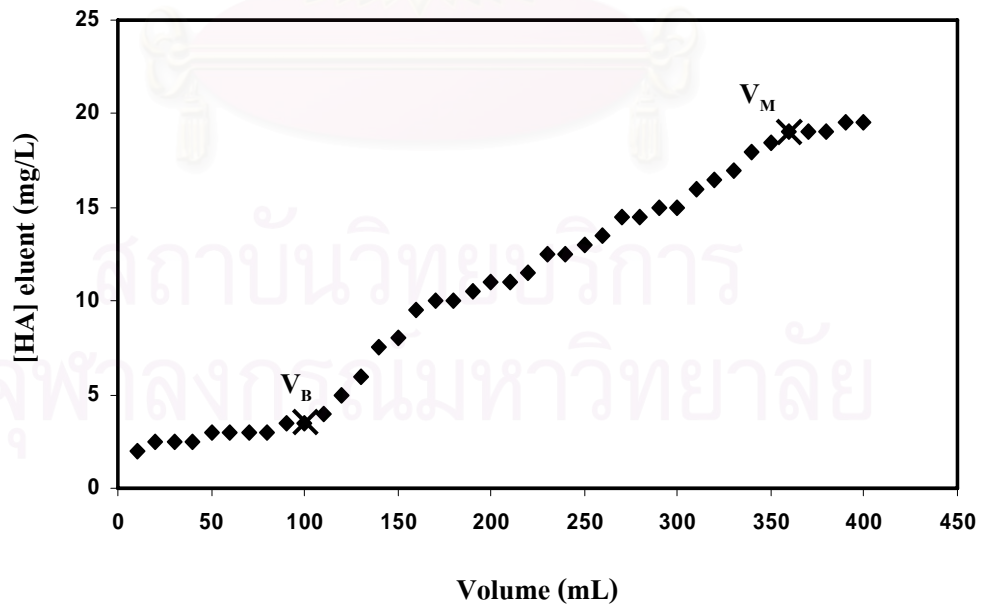


Figure 4.16 Breakthrough curve of RHA-NH₂ column (synthetic water); mass of adsorbent = 0.5 g, initial concentration = 20 mg/L, flow rate = 1.5 mL/min, pH = 6.0.

Figure 4.17 shows the capacity of HA adsorption onto RHA which is found to decrease, in general, with increasing number of loading of HA solution, there was hardly any adsorption at over the 9th fraction corresponding to 90 mL of HA solution (V_M). During the initial stage of adsorption, a large number of vacant surface sites are available for adsorption, but there was no further rise probably due to the limited active sites available to adsorb HA on the RHA surface. The cumulative adsorption capacity of RHA is illustrated in Figure 4.17, it is found that the adsorption reached saturation. Therefore, the maximum adsorption capacity of 2.10 mg/g was obtained. This maximum adsorption capacity is lower than that obtained from the calculation by Langmuir adsorption equation (Q_0) which is 2.72 mg/g. It could be concluded that the adsorption by the batch method is more efficient than that of the column method because in the batch method the equilibrium was reached.

The capacity of HA adsorption onto RHA-NH₂ is illustrated in Figure 4.18, where a small decrease was found, in general, with increasing number of loading of HA solution. The cumulative adsorption capacity (Figure 4.18) showed that the saturation was reached at over the 36th fraction that corresponds to 360 mL of HA solution (V_M). The observed maximum adsorption capacity (approximately found to be 7.50 mg/g) is close to that obtained from the calculation by Langmuir adsorption equation (Q_0) which is 8.20 mg/g. According to result, the RHA-NH₂ is a suitable adsorbent for the column system.

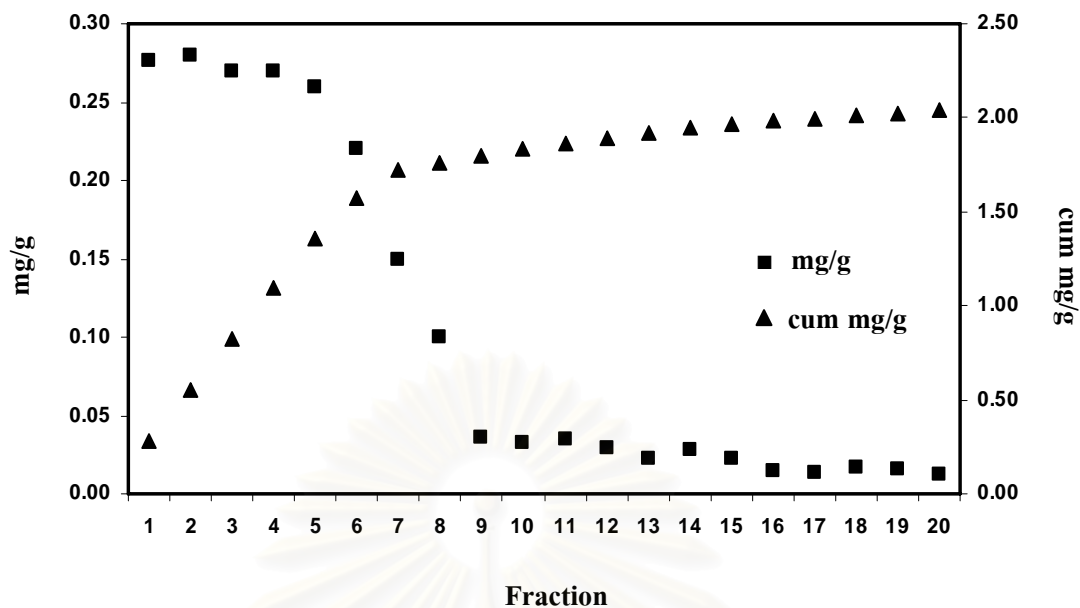


Figure 4.17 Relationship between number of fraction of loading HA solution and adsorption capacity (mg/g) with cumulative adsorption capacity by RHA (cum mg/g).

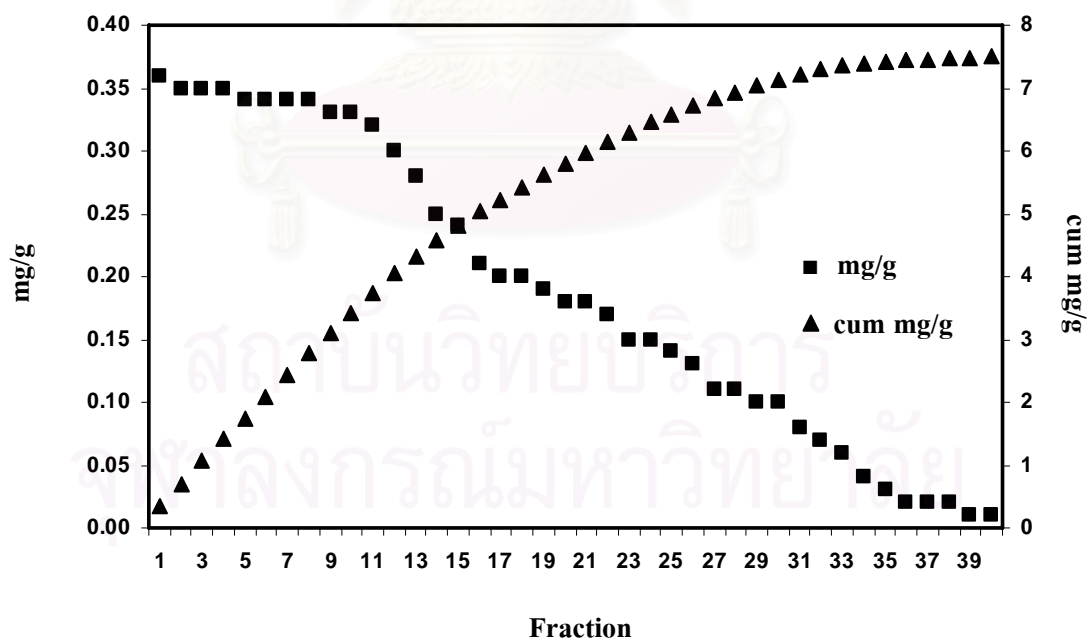


Figure 4.18 Relationship between number of fraction of loading HA solution and adsorption capacity (mg/g) with cumulative adsorption capacity by RHA-NH₂ (cum mg/g).

4.5 Application for real sample

In order to illustrate the potential application of using the prepared sorbents for real sample, surface water was collected from Chulalongkorn Pond and spiked with HA stock solution to obtain the final concentration of 20 mg/L. The breakthrough curves of real sample are illustrated in Figure 4.19 and 4.20. The first point on the curve is the breakthrough volume (V_B). The results showed that V_B are 50 and 100 mL for RHA and RHA-NH₂, respectively. These breakthrough volumes are similar to that obtained from the synthetic sample presented previously. It reveals that concomitants in surface water did not affect the adsorption of HA by the sorbents.

A second point on the shape of the breakthrough is the maximum sampling volume (V_M). It is found that V_M of HA solution are 110 and 370 mL for RHA and RHA-NH₂, respectively. The obtained experimental data from real sample are slightly lower than that obtained from the synthetic water.

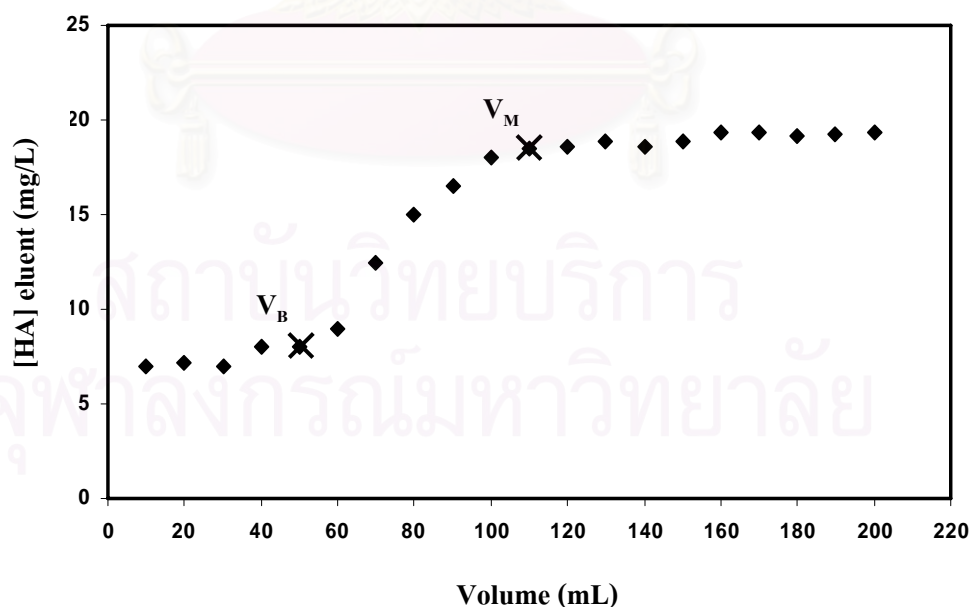


Figure 4.19 Breakthrough curve of RHA column (surface water); mass of adsorbent = 0.5 g, initial HA concentration = 20 mg/L, flow rate = 1.5 mL/min, and pH = 6.0.

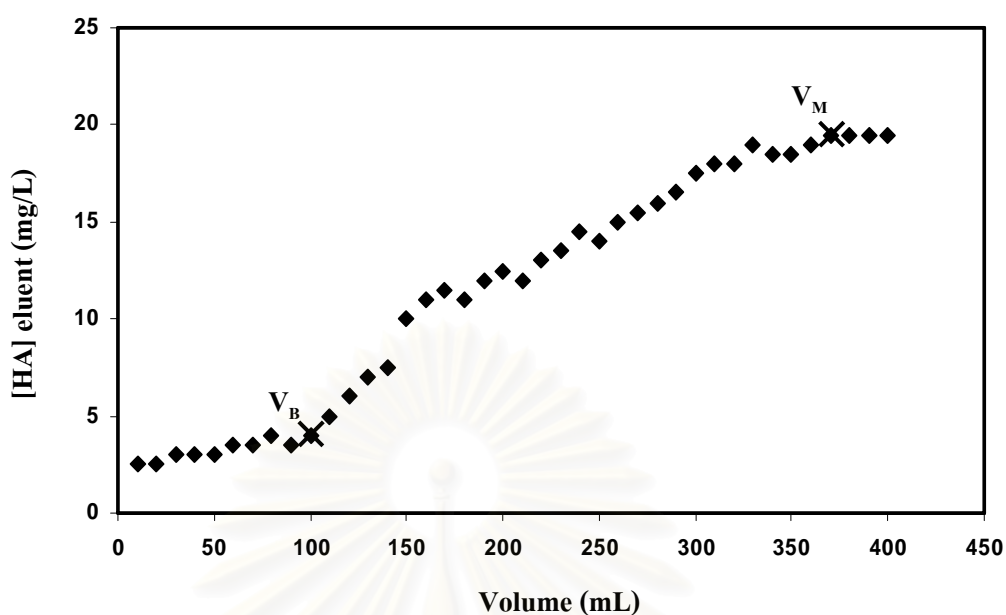


Figure 4.20 Breakthrough curve of RHA-NH₂ column (surface water); mass of adsorbent = 0.5 g, initial concentration = 20 mg/L, flow rate = 1.5 mL/min, and pH = 6.0.

Figure 4.21 shows the capacity of HA adsorption onto RHA which is found to decrease, in general, with increasing number of loading of HA solution, there was hardly any adsorption at over the 13th fraction. The cumulative adsorption capacity of RHA (Figure 4.21) is found that the adsorption reached saturation. Therefore, the maximum adsorption capacity of 2.0 mg/g was obtained. This maximum adsorption capacity is very near to that obtained calculation from synthetic water adsorption which is 2.1 mg/g.

The capacity of HA adsorption onto RHA-NH₂ was illustrated in Figure 4.22, where a small decrease was found, in general, with increasing number of loading of HA solution. The cumulative adsorption capacity (Figure 4.22) shows that the saturation was reached at over the 37th fraction. The observed maximum adsorption capacity is 6.7 mg/g that is close to that obtained from the calculation from synthetic water adsorption which is 7.5 mg/g. The results indicated that the obtained experimental data from real sample are not significantly different from synthetic water. According to result, both adsorbents can be applied for real sample.

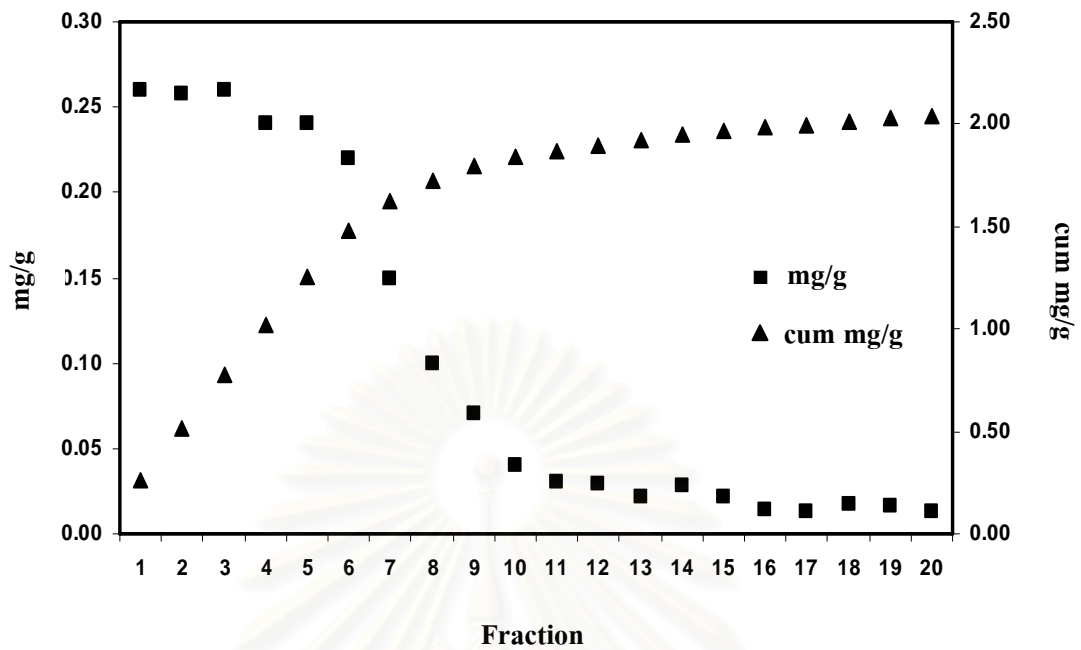


Figure 4.21 Relationship between number of fraction of loading surface water and adsorption capacity with cumulative adsorption capacity by RHA column.

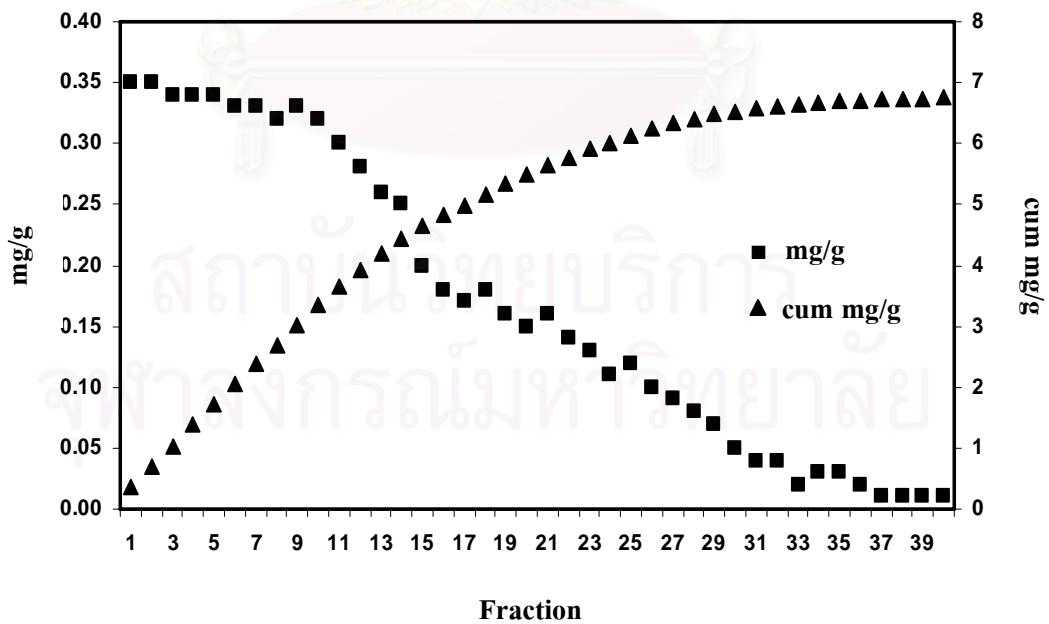


Figure 4.22 Relationship between number of fraction of loading surface water and adsorption capacity with cumulative adsorption capacity by RHA-NH₂ column.

Table 4.5 Comparison of experimental data from adsorption studies in column method between RHA and RHA-NH₂

Sample	Adsorbent	V _B (mL)	V _M (mL)	Maximum adsorption capacity (mg/g)
Synthetic water	RHA	50	90	2.1
	RHA-NH ₂	100	360	7.5
Real water (surface water)	RHA	50	110	2.0
	RHA-NH ₂	100	370	6.7

* mass of adsorbent = 0.5 g, initial concentration = 20 mg/L, flow rate = 1.5 mL/min, and pH = 6.0.

The comparison of obtained experimental data from adsorption studies of RHA and RHA-NH₂ columns is illustrated in Table 4.5. The results show that V_B, V_M and maximum adsorption capacity of RHA-NH₂ were higher than that of RHA, it is indicated that RHA-NH₂ is a better adsorbent than RHA for using in column method.

4.6 Comparison of adsorption efficiency with activated carbon

The comparative efficiency of the prepared adsorbents and two commercial activated carbons was investigated by agitating the working standard solution with adsorbents in the same condition. The adsorption efficiencies are given in Table 4.5.

Table 4.6 Comparison of adsorption efficiency with commercial activated carbon

Adsorbent	BET surface area (m ² /g)	Adsorption capacity (mg/g)*
RHA	192.13	1.8±0.1
RHA-NH ₂	22.88	7.9±0.4
Powder activated carbon, PAC	583.74	8.1±0.1
Granular activated carbon, GAC	25.50	3.7±0.2

*Mean value ± SD (n = 3)

Figure 4.23 presents a comparison of the adsorption efficiency of HA on RHA, RHA-NH₂, and 2 types of commercial activated carbon (PAC and GAC). It is seen that the prepared adsorbents and activated carbon samples exhibited different adsorption capacity. The RHA exhibited the lowest adsorption capacity. The PAC showed the highest HA adsorption at 8.1±0.1 mg/g which is in the same order to the adsorption capacity of RHA-NH₂ (7.9±0.4 mg/g). The highest capacity is due to the highest BET surface area of PAC (Table 4.6). It is suggested that if we can develop the preparation mode of RHA-NH₂ for increasing surface area for example by grinding into smaller particle, the sorption capacity would be improved. The order of HA adsorption capacities turned out to be PAC ~ RHA-NH₂ > GAC > RHA. The result shows that the adsorbabilities of PAC and RHA-NH₂ are not significantly different. According to the result, we assumed that RHA-NH₂ can be used instead of the commercial activated carbon, especially the GAC.

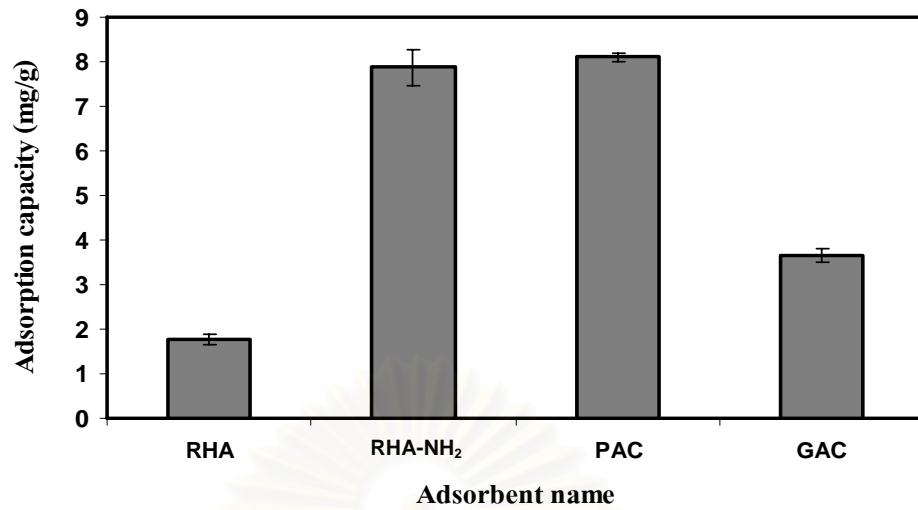


Figure 4.23 Adsorbability of HA onto different adsorbents.

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CHAPTER V

CONCLUSION

An agricultural waste, rice husk ash (RHA), is found to be a suitable adsorbent for adsorption of humic acids (HA) from water. The surface modification of RHA with amino group produced a novel adsorbent (RHA-NH₂) for increase the adsorption capacity. The optimum conditions observed by the batch method of these studies are summarized in Table 5.1.

Table 5.1 Optimum condition for HA adsorption on RHA and RHA-NH₂

	RHA	RHA-NH ₂
Equilibrium time (min)	60	30
Optimum pH	3.0	3.0-4.0
Maximum adsorption capacity (mg/g), at pH 6.0	2.72	8.20

The equilibrium between the adsorbate in the solution and on RHA and RHA-NH₂ was practically achieved in 30 and 60 min, respectively. The studies of adsorption demonstrated that RHA and RHA-NH₂ can be used as adsorbents for the removal of HA under acidic pH conditions (pH < 5.0), and pH 3.0 was found to be the optimum pH for both adsorbents. Equilibrium adsorption of HA by RHA followed typical adsorption isotherms and fits both the Langmuir and Freundlich adsorption isotherms. Whereas, the adsorption behavior of RHA-NH₂ was the best represented by the Langmuir isotherm. The calculated maximum adsorption capacities of RHA and RHA-NH₂ were 2.72 and 8.20 mg/g, respectively, at pH 6.0. In the column system, the results revealed the feasibility of using the adsorbents derived from rice husk in water treatment. The comparison adsorption efficiency with commercial adsorbents showed that the adsorbabilities of powder activated carbon (PAC) and RHA-NH₂ are not significantly different. Therefore, RHA-NH₂ can be used instead of commercial activated carbon. The adsorbents were applied for humic acids removal from surface water. The electrostatic attraction and surface complex formation are possible for the adsorption of HA on the RHA and RHA-NH₂ surface.

Suggestions for future work

This present study was able to apply for water treatment. The effect of major interfering ions in the water treatment process as well as the effect of various parameters on the column system and the comparison of adsorption efficiency with other commercial adsorbents such as silica gel and chitosan should be studied further, as well as the study of the competitive adsorption by other dissolved organic matters present in real water sample.



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