สมบัติการดูดซับและการคืนสภาพของถ่านกัมมันต์สำหรับกรดซาลิไซลิกและกรดฮิวมิกที่ละลายในน้ำ

นายวัลลภ คงนะ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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ADSORPTIVE PROPERTY AND REGENERATION OF ACTIVATED CARBON FOR DISSOLVED SALICYLIC ACID AND HUMIC ACIDS IN WATER

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A Thesis Submitted in Partial Fulfillment of the Requirements
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นายวัลลภ คงนะ : สมบัติการดูดซับและการคืนสภาพของถ่านกัมมันต์สำหรับกรดซาลิไซลิกและกรดฮิวมิกที่ละลายในน้ำ. (ADSORPTIVE PROPERTY AND REGENERATION OF ACTIVATED CARBON FOR DISSOLVED SALICYLIC ACID AND HUMIC ACIDS IN WATER) อ.ที่ปรึกษาวิทยานิพนธ์หลัก : ผศ.ดร.อภิชาติ อิ่มยิ้ม, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม : ผศ.ดร.ณรงค์ ประไพรักษ์สิทธิ์, 52 หน้า

งานวิจัยนี้ได้ทำการศึกษาภาวะที่เหมาะสมในการดูดซับกรดซาลิไซลิกและกรดฮิวมิกแบบแยกกันและแบบพร้อมกันบนถ่านกัมมันต์แบบเกล็ด โดยมีตัวแปรได้แก่ พีเอชเริ่มต้นของสารละลาย ความเข้มข้นเริ่มต้นของสารละลายกรดซาลิไซลิกและกรดฮิวมิก และระยะเวลาในการดูดซับ และได้ทำการศึกษาการคืนสภาพของถ่านกัมมันต์แบบเกล็ด โดยมีตัวแปรได้แก่ ชนิดของตัวชะ และระยะเวลาในการชะ จากการทดลองพบว่า ภาวะที่เหมาะสมในการดูดซับกรดซาลิไซลิกและกรดฮิวมิกแบบแยกกันบนถ่านกัมมันต์แบบเกล็ด คือ พีเอชเริ่มต้นของสารละลายเท่ากับ 1.0 และ 4.0 ตามลำดับ ความเข้มข้นเริ่มต้นของสารละลายกรดซาลิไซลิกและกรดฮิวมิกเท่ากับ 400 และ 100 มิลลิกรัมต่อลิตร ตามลำดับ ระยะเวลาในการดูดซับ 4 ชั่วโมง พฤติกรรมการดูดซับที่เกิดขึ้นเป็นไปตามแบบจำลองการดูดซับของแลงเมียร์และฟรุนด์ลิช โดยมีความสามารถในการดูดซับกรดซาลิไซลิกและกรดฮิวมิกสูงสุดเท่ากับ 175.4 และ 16.3 มิลลิกรัมต่อกรัม ตามลำดับ และอัตราเร็วในการดูดซับสามารถทำนายด้วยสมการอัตราการเกิดปฏิกิริยาอันดับสองเทียม ภาวะที่เหมาะสมในการดูดซับกรดซาลิไซลิกและกรดฮิวมิกแบบพร้อมกันบนถ่านกัมมันต์ คือ พีเอชเริ่มต้นของสารละลายเท่ากับ 4 ความเข้มข้นเริ่มต้นของสารละลายกรดซาลิไซลิกและกรดฮิวมิกเท่ากับ 400 และ 100 มิลิกรัมต่อลิตร ตามลำดับ โดยมีความสามารถในการดูดซับกรดซาลิไซลิกและกรดฮิวมิกสูงสุดเท่ากับ 101.1 และ 12.2 มิลลิกรัมต่อกรัม ตามลำดับ และระยะเวลาในการดูดซับ 4 ชั่วโมง ภาวะที่เหมาะสมในการคืนสภาพถ่านกัมมันต์ คือ ตัวชะชนิดสารละลายโซเดียมไฮดรอกไซด์เข้มข้นร้อยละ 5 ในเอทานอลร้อยละ 10 ในน้ำ และระยะเวลาในการชะ 1 ชั่วโมง โดยมีเปอร์เซ็นต์การชะกรดซาลิไซลิกและกรดฮิวมิกออกจากถ่านกัมมันต์เท่ากับ 81.6 และ 62.3% ตามลำดับ การคืนสภาพให้กับถ่านกัมมันต์และนำถ่านกัมมันต์กลับมาใช้ซ้ำนั้นมีความเป็นไปได้ และประสิทธิภาพการดูดซับจะลดลงเมื่อจำนวนครั้งที่ใช้ซ้ำมากขึ้น

ภาควิชา..................เคมี................. ลายมือชื่อนิสิต..
สาขาวิชา................เคมี.................. ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก...
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WANLOP KHONGNA: ADSORPTIVE PROPERTY AND REGENERATION OF ACTIVATED CARBON FOR DISSOLVED SALICYLIC ACID AND HUMIC ACIDS IN WATER. THESIS ADVISOR: ASST.PROF.APICHAT IMYIM, Ph.D., THESIS CO-ADVISOR: NARONG PRAPHAIRAKSIT, Ph.D., 52 pp.

In this work, optimal conditions for individual adsorption and simultaneous adsorption of salicylic acid and humic acids onto granular activated carbon were studied. Adsorption conditions were optimized for batch method such as initial pH of solution, initial concentration and contact time. Optimal conditions for desorption of salicylic acid and humic acids from granular activated carbon were studied. Desorption conditions were optimized for batch method such as eluent type and contact time. The optimal initial pH for individual adsorption of salicylic acid and humic acids were 1.0 and 4.0, respectively. The optimal initial concentrations of salicylic acid and humic acids were 400 and 100 ppm, respectively while the equilibrium time of salicylic acid and humic acids was reached within 4 hours. Adsorption behaviors of salicylic acid and humic acids followed Langmuir and Freundlich adsorption isotherm. The maximum adsorption capacity of the granular activated carbon for adsorption of salicylic acid and humic acids were 175.4 and 16.3 mg/g, respectively. The rate of adsorption could be predicted with the pseudo second order model. The optimal conditions for simultaneous adsorption of salicylic acid and humic acids were found as follows, initial pH 4.0, initial concentration of salicylic acid and humic acids were 400 and 100 mg/L, respectively. The maximum adsorption capacities for salicylic acid and humic acids were 101.1 and 12.2 mg/g, respectively and the equilibrium time was reached within 4 hours. Optimal conditions for desorption of salicylic acid and humic acids from granular activated carbon were found to be 5% NaOH in 10% ethanol/water as eluent and 1 hour desorption time. Elution of salicylic acid and humic acids from granular activated carbon were 81.6 and 62.3%, respectively. A number of reuse of sorbent after regeneration was possible and the adsorption efficiency decreased gradually.

Department……….Chemistry……….Student’s signature…………………………......
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LIST OF SYMBOLS AND ABBREVIATION

nm	Nanometer
^{o}C	Degree Celsius
µm	Micrometer
g	Gram
mg	Milligram
L	Liter
mL	Milliliter
µmol	Micromole
MHz	Megahertz
K	Kelvin
kHz	Kilohertz
UV-Vis	Ultra violet-visible
M	Molarity
min	minute

CHAPTER I

INTRODUCTION

1.1 Statement of the problem

Humic substances are organic compounds dissolved in water resulting from the decomposition of plant and animal materials. Humic substances in natural water can be transformed to disinfection byproducts (DBPs) when reacted with disinfectants such as chlorine during chlorination step in drinking water treatment [1]. That may pose cancer risks to human health. Therefore, the removal of humic substances becomes important to control the amount of humic substances in natural water before treating with disinfectants.

Adsorption on activated carbon is one of efficient methods for the removal of humic substances. Activated carbon is a very effective adsorbent due to its highly developed porosity and large surface area. Desorption processes are also important for adsorbent regeneration and reuse in economical aspect of drinking water treatment.

Humic substances can be divided into three fractions, i.e., humic acids, fulvic acids and humin [2]. In this study, salicylic acid was chosen to study adsorption onto activated carbon and desorption because its functional groups were similar to those of humic substances and it was widely used as a model compound for fulvic acids.

1.2 Objectives

(1) To study optimal conditions for adsorption and desorption of salicylic acid and humic acids on granular activated carbon.

(2) To develop simple regeneration methods of granular activated carbon and to evaluate the possibility of its reuse.

1.3 Scope of this research

The following items are concerned in this study:

(1) The investigation of the optimal conditions for adsorption of salicylic acid and humic acids on granular activated carbon by varying the following parameters: contact time, initial pH and initial concentration.

(2) The investigation of the optimal conditions for desorption of salicylic acid and humic acids from granular activated carbon by varying eluent type and elution time.

(3) The studies of simultaneous adsorption of salicylic acid and humic acids on granular activated carbon under optimal adsorption conditions.

(4) The studies of simultaneous desorption of salicylic acid and humic acids from granular activated carbon under optimal desorption conditions.

(5) The regeneration and reuse of granular activated carbon.

1.4 The benefits of this research

The following knowledge and procedure would be achieved.

- Simultaneous adsorption and desorption behaviors of salicylic acid and humic acids onto granular activated carbon.

- A method for regeneration and reuse of granular activated carbon in humic substances removal.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Humic substances

2.1.1 Characteristics and background

Humic substances are ubiquitous organic constituents present in a wide range of soils, peats, sediments and aquatic ecosystems. They are degradation resistant materials, formed during the decomposition of vegetation. Humic substances are leached from decaying plant materials or humus on the land surface and transported by surface and subsurface water in the soluble or colloidally dispersed form to subsurface sand environments or to brackish or saline water bodies where flocculation or precipitation of the humic substances is triggered by various physical chemical mechanisms [3]. Humic substances have high molecular mass. Molecular mass ranges from a few hundred Dalton for fulvic acids to ten of thousands Dalton for humic acids and humin fractions. Humic substances can be divided into three components; fulvic acids, humic acids and humin as shown in Figure 2.1.

- Fulvic acids are the most soluble fraction of humic substances that are soluble in water at all pH value. They are yellow-brown in color. The structure and chemical composition of fulvic acids depends on the source of material and environment. Fulvic acid may have different amounts of aromatic ring and aliphatic chains with different numbers of carboxyl, carbonyl, alcoholic and phenolic, phosphate, sulfate, amino group, amide, alkyl and/or disulfide functional groups [4]. The molecular size of fulvic acids is found in the range of approximately 1,000 to 5,000 Dalton [5].

- Humic acids are the fraction of humic substances that are soluble in water at pH value over two. They can be extracted from soil by various reagents. They are dark brown to black in color. The major functional groups in humic acid are carboxyl, phenolic, carbonyl and hydroxyl groups connected with the aliphatic or aromatic carbons in the macromolecules [6]. The existence of carboxyl and phenolic groups causes humic acids to have negative charges in aqueous solution [7]. The solubility of humic acids in aqueous media also depends on the number of –COOH and –OH group. The molecular size of humic acids is found in the range of approximately 50,000 to 500,000 Dalton [5].

- Humin is the fraction of humic substances that is insoluble in water at all pH. They are black in color.

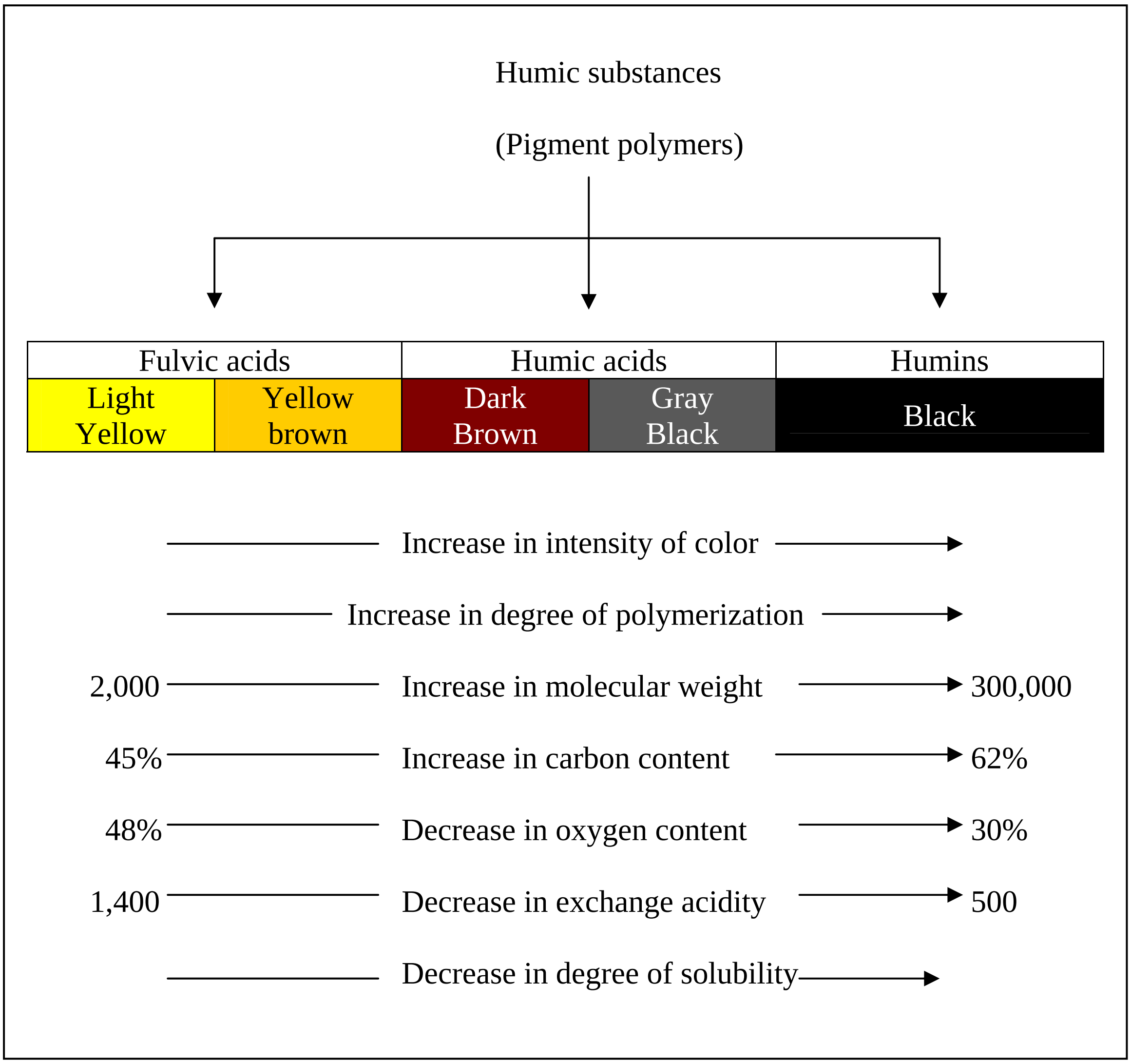

Figure 2.1 Chemical properties of humic substances [8].

2.1.2 Humic substance properties and structure

Humic substances are comprised mainly of aromatic, aliphatic, phenolic, quinonic and N-derived components, which are covalently bound through C-C, C-O-C and N-C bonds. They have an abundance of oxygen containing functional groups (carboxyl, phenol, alcoholic, ketone, ester, and ether) which dominate their properties and structure. Elemental analyses of humic acids, fulvic acids, and humins from all over the world are essentially consistent. Their contents usually range from ~40 to 50 % C and ~40 to 50 % O for fulvic acids; ~50 to 65 % C and ~30 to 40 % O for humic acids. The H, N and S contents range from ~3 to 7 %, ~0.8 to 4.3 % and ~0.1 to 3.6 % respectively, in all of the fractions. The most acceptable hypothetical structure of humic acids model was known as Stevenson humic acids model in Figure 2.2 [4].

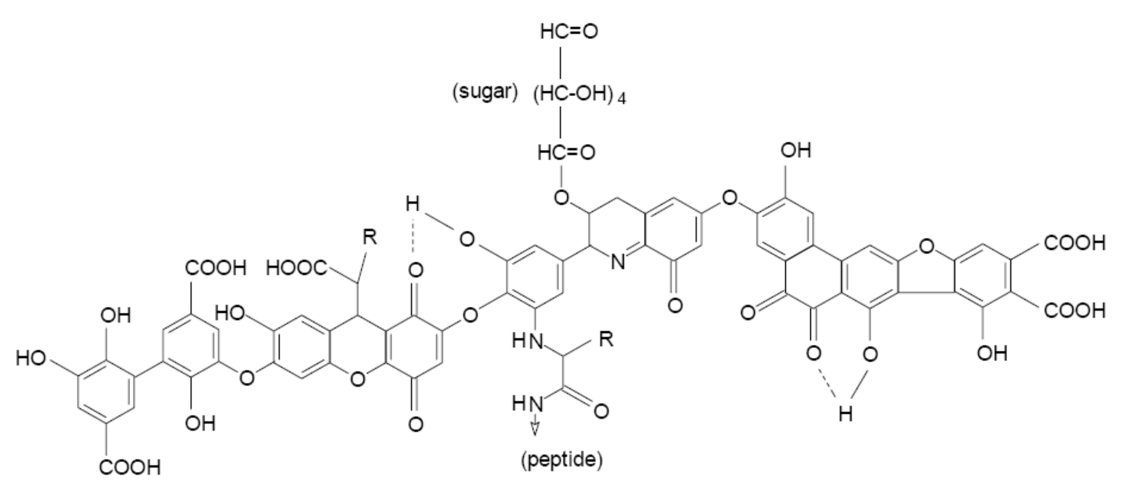

Figure 2.2 Model structure of humic acids [4].

2.1.3 Extraction of humic substances

Extraction of humic substances from soils and sediments is often the first task that confronts the investigator. The classical method of fractionation of humic substances following extraction is based on differences in solubility in aqueous solutions at various pH levels and electrolyte concentrations and in alcohol as shown in Figure 2.3 [3].

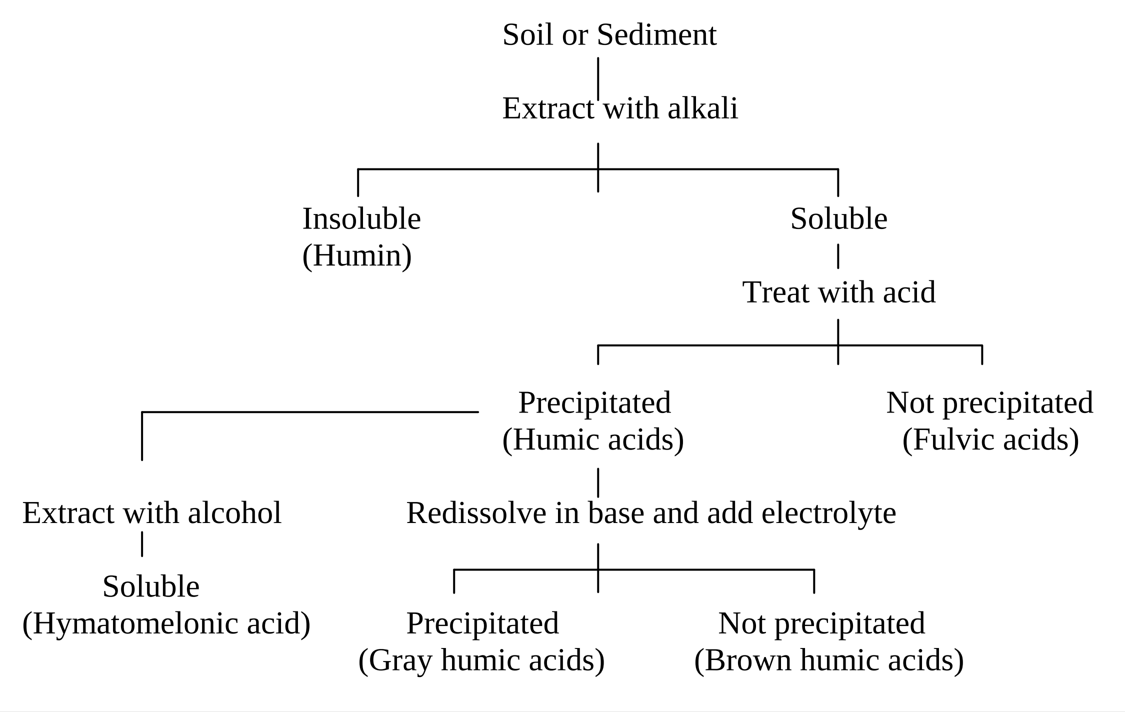

Figure 2.3 Fractionation of humic substances [3].

2.1.4 Determination of humic substances in water

Ultra-violet (UV) absorption at a wavelength of 253.7 nm (often rounded off to 254 nm) is used to provide an indication of the aggregate concentration of UV-absorbing organic constituents, such as humic substances and various aromatic compounds [8]. Humic aromatic compounds and molecules with conjugated double bonds absorb UV light, whereas simple aliphatic acids, alcohol, and sugars do not absorb UV light. Organic compounds that are aromatic or that have conjugated double bonds absorb light in the ultraviolet wavelength region. Therefore, UV absorbance is a well-known technique for measuring the presence of naturally occurring organic matter such as humic substances.

2.1.5 Environmental effects

Humic substances can easily be transported in the aqueous phase through soil and other natural waters and it is well established that they play an important role in the distribution of contaminants in the environment. Contaminant bound humic substances are highly relevant to their bioavailability and toxicity. However, one of the concerns for the environmental problem caused by the presence of humic substances in natural water is the formation of disinfection by-products (DBPs) during disinfection by chlorine in drinking water treatment that are carcinogenic products. Chlorine can combine with humic substances in water to form chlorinated organic compounds, such as chloroform, other low-molecular-weight disinfection by-products (e.g., haloacetonitriles, haloacids, haloaldehydes, haloketones, chloropicrin, and cyanogens chloride) and high-molecular-weight chlorinated compounds.

2.1.6 Conventional method for removal of humic substances

Very low levels of humic substances in drinking water are suspected of contributing to cancer and other maladies. Water disinfection processes, which by their nature involve chemically rather severe conditions, particularly of oxidation, have a tendency to produce disinfection by-products. Some of these are chlorinated organic compounds produced by chlorination of organics in water, especially humic substances. Removal of humic substances to very low levels prior to chlorination has been found to be effective in preventing trihalomethane formation. Another major class of disinfection by-products consists of organo-oxygen compounds such as aldehydes, carboxylic acids, and oxoacids.

2.1.6.1 Adsorption with activated carbon

Activated carbon is commonly used in drinking water treatment, waste water treatment, etc. Its main use is the removal of pollutants such as pesticides, industrial chemicals, tastes and odors [6]. The adsorption of compounds to the activated carbon is influenced by the structural and the chemical characteristics of the carbon surface [7]. However, one reason for the effectiveness of this material as an adsorbent is its tremendous surface area. A solid cubic foot of carbon particles can have a combined pore and surface area of approximately 10 square miles. Although interest is increasing in the use of powdered activated carbon for water treatment, granular activated carbon is currently more widely used. It can be employed in a fixed bed, through which water flows downward. Accumulation of particulate matter requires periodic backwashing. An expanded bed in which particles are kept slightly separated by water flowing upward can be used with less chance of clogging.

2.1.6.2 Membranes

Membrane filtration is frequently used for the purification of water. Membranes are thin, typically less than 1 mm thick, and vary in their composition and the sizes of the pores through which water flows. Membranes are made from a variety of materials, including organic polymers, such as cellulose acetate, and inorganic ceramics composed of silicon and metal oxides fired at high temperatures. Membrane filtration uses high pressures, which increase with decreasing pore size. Microfiltration is usually conducted at pressures below 5 atm, ultrafiltration at 2-8 atm, nanofiltration at 5-15 atm, and reverse osmosis or hyperfiltration at 15-100 atm. To accommodate high pressures, membranes are usually configured as hollow fibers. Typically, contaminated water flows through the inside of the fiber, purified water flows to the outside of the fiber, and water concentrated in contaminants exits from the downstream end of the fiber. This configuration also enables continuous flushing of the internal membrane surface to aid in removal of retained impurities. Some systems in which the filtration device is immersed in the wastewater operated with the flowing from the outside to the inside of the hollow fibers [9].

2.1.6.3 Coagulation

Coagulation is a common unit process used to remove humic substances. The coagulants that are the most widely used in water treatment are aluminum and iron salts. Aluminum salts are employed more frequently than iron salts because they are usually cheaper. The water must contain sufficient alkalinity in order for it to react with aluminum sulfate to produce the hydroxide flocculation. Usually, for the pH ranges involved, the alkalinity is in the form of a bicarbonate ion. In the case of water that dose not have sufficient alkalinity to react with alum, alkalinity must be added. Usually alkalinity in the form of a hydroxide ion is added by the addition of calcium hydroxide. Alkalinity may also be added in the form of a carbonate ion by the addition of sodium carbonate. Most water has sufficient alkalinity, so no chemical needs to be added other than aluminum sulfate. The optimum pH range for alum is from about 4.5-8.0. Alum sulfate is available in dry or liquid form; however, the dry form is more common. The dry chemical may be in granular, powder, or lump form; the granular form being the one most widely used [10].

2.1.6.4 Anion exchange

Anion exchange based upon the reversible exchange of ions between solid phase (the anion exchange resin) and water phase. The most important mechanism in anion exchange process for humic substances removal is the exchange of ion, e.g. exchange of humic substances and chloride ions rather than physical adsorption [11].

2.2 Disinfection and disinfection by-products

The disinfection process has been routinely carried out since the dawn of the 20th century to eradicate and inactivate the pathogens from water used for drinking purpose. Disinfectants in addition to removing pathogens from drinking water, serve as oxidants in water treatment. They are also used for removing taste and color; oxidizing iron and manganese; improving coagulation and filtration efficiency; preventing algal growth in sedimentation basins and filters, and preventing biological regrowth in the water distribution system. Chlorine and its compounds are the most commonly used disinfectants for water treatment. Chlorine’s popularity is not only due to lower cost, but also to its higher oxidizing potential, which provides a minimum level of chlorine residual throughout the distribution system and protects against microbial recontamination.

The application of disinfection agents to drinking water reduces the microbial risk but poses chemical risk in the form of their by-products. The disinfection by-products are formed when the disinfectant reacts with natural organic matter and/or inorganic substances present in water. More than 250 different types of disinfection by-products have already been identified. Table 2.1 lists major classes of disinfection by-products formed by various disinfectants. The disinfection by-products concentrations may vary in orders of magnitude during different disinfection processes. The formation of chlorinated disinfection by-products in drinking water like trihalomethanes has emphasized the need for exploring alternate disinfectants and new treatment technologies. Because organic/inorganic substances act as precursors for disinfection by-products, their removal prior to disinfection has proven to be an effective method for reducing chlorinated disinfection by-product formation potential. The natural organic matter can be partially removed using a conventional treatment (coagulation, flocculation, sedimentation and filtration) or by combining/replacing its components with more efficient processes such as granular activated carbon filtration, enhanced coagulation and membrane filtration. Another effective method to control chlorinated disinfection by-products in drinking water is the use of alternative disinfectants (ozone, chloramines, chlorine dioxide and more recently ultraviolet light) alone or in combination with chlorine. The applications of various disinfectants, as well as their costs, disinfection efficiencies and stability in distribution systems are summarized in Table 2.2.

Table 2.1 Important groups of disinfection by-products produced using different types of disinfectants [12]

Class of disinfection by-products	Common example	Chlorine	Ozone	ClO_2	Chloramines
Trihalomethanes (THMs)	Chloroform	✓	✓		✓
Other haloalkanes		✓			
Haloalkenes		✓			
Haloacetic acids (HAAs)	Chloroacetic acid	✓			✓
Haloaromatic acids		✓			
Other halomonocarboxylic acids		✓			✓
Unsaturated halocarboxylic acids		✓			✓
Halodicarboxylic acids		✓			✓
Halotricarboxylic acids		✓			
Mx and analogues		✓		✓	✓
Other halofuranones		✓			
Haloketones		✓	✓	✓	
Haloacetonitriles (HANs)	Chloroacetonitrile	✓	✓		
Other halonitrile	Cyanogen chloride	✓			✓
Haloaldehyde	Chloral hydrate	✓			✓
Haloalcohols		✓			✓
Phenols	2-Chlorophenol	✓	✓		
Halonitromethane	Cloropicrin	✓			
Inorganic compounds	Bromate		✓	✓	
Aliphatic aldehyde	Formaldehyde	✓	✓	✓	
Other aldehydes		✓	✓	✓	
Ketones (aliphatic and aromatic)	Acetone	✓	✓	✓	
Carboxylic acids	Acetic acid	✓	✓	✓	
Aromatic acids	Benzoic acid	✓	✓	✓	
Aldo and Ketoacids			✓	✓	
Hydroxy acids		✓	✓		
Other		✓	✓	✓	✓

NB: Major classes of disinfection by-products are shown in bold

Table 2.2 Basic information of disinfectants [13]

Issue		**Chlorine**	**Chloramine**	**Chlorin dioxide**	**Ozone**	**Ultraviolet radiation**
Application		Most common	Common	Occasional	Common	Emerging use
Cost		Lowest	Moderate	High	High	Extremely high
Disinfection efficiency	Bacteria	Excellent	Good	Excellent	Excellent	Good
	Viruses	Excellent	Fair	Excellent	Excellent	Fair
	Protozoa	Fair to poor	Poor	Good	Good	Excellent
	Endospores	Good to poor	Poor	Fair	Excellent	Fair
Organisms regrowth		Unlikely	Unlikely	likely	More likely	More likely
Limits on free residual		4 mg/L	4 mg/L	0.8 mg/L	-	-
By-products	Regulated	4 THMs, HAAs	Traces of THMs and HAAs	Chlorite	Bromate	None
	Unregulated	Many	Many: cyanogen halides	Many: chlorate	Biodegradable organics	None known
Oxidation		Strong	Weak	Selective	Strongest	None
Odor and taste removal		Excellent	Good	Excellent	Good to poor	None
Stability		Stable	Stable	Unstable	Unstable	Unstable

2.3 Activated carbon

2.3.1 Characteristics and background

Activated carbon is carbon that has been processed to make it extremely porous. Their preparation involves two main steps: the carbonization of the carbonaceous raw material at temperatures below 800^{o}C in an inert atmosphere and the activation of the carbonized product. Thus, all carbonaceous materials can be converted into activated carbon, although the properties of the final product will be different, depending on the nature of the raw material used, the nature of the activating agent, and the conditions of the carbonization and activation process. Activated carbon has a very wide range of pore sizes, from the angstrom scale of micropores to the micrometer scale of macropores. Due to its high porous structure, just 1 gram of activated carbon has a surface area ranging from 500 to 2500 m^2. The complex internal surface area is usually divided into three components. Channels and pores with diameters less than 2 nm are commonly known as micropores; these micropores generally contain the largest portion of the carbon's surface area. On the other hand, pores with diameters between 2 and 50 nm are know as mesopores, and pores with diameters greater than 50 nm are defined as macropores.

During the carbonization process, most of the noncarbon elements such as oxygen, hydrogen, and nitrogen are eliminated as volatile gaseous species by the pyrolytic decomposition of the starting material. The residual elementary carbon atoms group themselves into stacks of flat, aromatic sheets cross-linked in a random manner. These aromatic sheets are irregularly arranged, which leaves free interstices. These interstices give rise to pores, which make activated carbons excellent adsorbents. During carbonization these pores are filled with the tarry matter or the products of decomposition or at least blocked partially by disorganized carbon. This pore structure in carbonized char is further developed and enhanced during the activation process, which converts the carbonized raw material into a form that contains the greatest possible number of randomly distributed pores of various sizes and shapes, giving rise to an extended and extremely high surface area of the product. The activation of the char is usually carried out in an atmosphere of air, CO_2 or stream in the temperature range of 800^oC to 900^oC. This results in the oxidation of some of the regions within the char in preference to other, so that as combustion proceeds, a preferential etching takes place. This results in the development of a large internal surface, which in some cases may be as high as 2500 m^2/g [14].

Activated carbons have a microcrystalline structure. But this microcrystalline structure differs from that of graphite with respect to interlayer spacing, which is 0.335 nm in the case of graphite and ranges between 0.34 and 0.35 nm in activated carbon. The orientation of the stacks of aromatic sheets is also different, being less ordered in activated carbon. The aromatic sheets in activated carbons contain free radical structure or structure with unpaired electrons. These unpaired electrons are resonance stabilized and trapped during the carbonization process, due to the breaking of bonds at the edges of the aromatic sheets, and thus, they create edge carbon atoms. These edge carbon atoms have unsaturated valencies and can, therefore, interact with heteroatoms such as oxygen, hydrogen, nitrogen, and sulfur, giving rise to different types of surface groups. The elemental composition of a typical activated carbon has been found to be 88% C, 0.5% H, 0.5% N, 1.0% S, and 6 to 7.0% O, with the balance representing inorganic ash constituents. The oxygen content of an activated carbon can vary, however, depending on the type of the source raw material and the conditions of the activation process. Activated carbon has a variety of surface groups as listed in Table 2.5.

Table 2.3 Surface groups on activated carbon and their effect on adsorbablility [15]

Groups	Adsorbability
Hydroxyl	Generally reduces adsorbability. Extent of decrease depends on structure of host molecules.
Amino	Effect similar to that of hydroxyl but somewhat greater. Many amino acids are not adsorbed to any appreciable extent.
Carbonyl	Effect varies according to host molecule. Glyoxylic acid more adsorbable than acetic but similar increase does not occur when introduced into higher fatty acids.
Double bonds	Variable effects as with carbonyl.
Halogen	Variable effect.
Sulfonic	Usually decreases adsorbability.
Nitro	Often increases adsorbability.

Adsorption on activated carbon is selective, favoring nonpolar over polar substances and in homologous series, generally improving with increasing boiling point. Adsorption is also improved with increased pressure and reduced temperature. Reversal of the physical adsorptive conditions (temperature, pressure, or concentration) more or less completely regenerates the carbon’s activity, and frequently allows recovery of both the carrier fluid and adsorbate. Compared with other commercial adsorbents, activated carbon has a broad spectrum of adsorptive activity, excellent physical and chemical stability, and ease of production from readily available, frequently wastes materials.

2.3.2 Production of activated carbon

Almost any carbonaceous raw materials can be used for the manufacture of activated carbon. Activated carbon is normally produced using two different processes.

2.3.2.1 Physical activation

The preparation involves two main steps: carbonization of the raw material at temperatures below 800^{o}C in an inert atmosphere, and activation of the carbonized product between 950 and 1000^{o}C. Thus, all carbonaceous materials can be converted into active carbons, although the properties of the final product will be different, depending upon the nature of the raw material used, the nature of the activating agent, and the conditions of the activation process. During carbonization most of the noncarbon element such as oxygen, hydrogen, nitrogen, and sulfur are eliminated as volatile gaseous products by the pyrolytic decomposition of the source raw material. The residual elementary carbon atoms group themselves into stacks of aromatic sheets cross-linked in a random manner.

2.3.2.2 Chemical activation

Impregnation with chemical such as acids like phosphoric acid or bases like potassium hydroxide or salts like zinc chloride, followed by carbonization at temperature in the range of 450 to 900^{o}C, it is believed that carbonization and activation step proceeds simultaneously in chemical activation. This technique can be problematic in some cases because, for example, zinc trace residues may remain in the end product. However, chemical activation is preferred over physical activation owing to the lower temperature and shorter time needed for activating material.

2.3.3 Classifications

Activated carbon is available in two main forms: powder activated carbon and granular activated carbon.

2.3.3.1 Powder activated carbon

Powder activated carbon is widely used for BOD and COD removal from wastewaters. It is also applied for treating wastewaters contaminated with phenol, volatile acids, aromatic and aliphatic organics. The average size of powder activated carbon is in the range of 15 to 25 µm.

2.3.3.2 Granular activated carbon

Granular activated carbon is widely used in drinking water and wastewater purification processes. It is used in form of a carbon bed, usually within a column, for water treatment. The water flows through the bed, where organic molecules present as contaminants are adsorbed on to the carbon surface. Granular activated carbons are either in form of crushed granules (coal or shell) or of pellets prepared by agglomerating pulverized powders with binders such as coal tar pitch. The average size of granular activated carbon is in the range of 0.6 to 4.0 mm.

2.3.4 Adsorption on activated carbon

Activated carbons are excellent and versatile adsorbents. Their important applications are the adsorptive removal of color, odor, and taste, and other undesirable organic and inorganic pollutants from drinking water, in the treatment of industrial wastewater; air purification in inhabited spaces, such as in restaurants, food processing, and chemical industrial; for the purification of many chemical, food, and pharmaceutical products; in respirators for work under hostile environments; and in a variety of gas-phase applications.

Carbon surface has a unique character. It has a porous structure which determines its adsorption capacity, it has a chemical structure which influences its interaction with polar and nonpolar adsorbates, it has active sites in the form of edge, dislocations and discontinuities which determine its chemical reactions with other atoms. Thus, the adsorption behavior of an activated carbon cannot be interpreted on the basis of surface area but prepared by different methods or given different activation treatments showing markedly different adsorption properties. The determination of a correct model for adsorption on activated carbon adsorbents with complex chemical structure is therefore, a complicated problem. A proper model must take into consideration both the chemical and the porous structure of the carbon, which includes the nature and concentration of the surface chemical groups, the polarity of the surface, the surface area, and the pore size distribution, as well as the physical and chemical characteristics of the adsorbate, such as its chemical structure, polarity, and molecular dimensions. In the case of adsorption from solutions, the concentration of the solution and its pH are also important additional factors.

In the adsorption of organics, the organic compounds present in water can be polar or nonpolar, so that not only electrostatic interactions but also dispersive interactions will play an important role. In addition, the hydrogen bonding is also an important consideration in the adsorption of certain polar organic molecules. The molecular dimensions of the organic molecules also have a wide variation. Thus, the porous structure of the activated carbon, which includes the existence of mesopores, shall also have an important consideration for the adsorption of essentially nonpolar organic molecules, because a certain proportion of the microporosity may not be accessible to very large organic molecules.

2.4 Adsorption theory

Adsorption is mass transfer that can generally be defined as the accumulation of materials at the interface between two phases. These phases can be any of the following combination: liquid-liquid, liquid-solid, gas-liquid, and gas-solid. In the adsorption process, molecules or atom or ions in a gas or liquid diffuse to the surface of a solid, where they bond with the solid surface or are held there by weak intermolecular forces. The adsorbed solutes are referred to as adsorbate, whereas the solid material is the adsorbent. Adsorption processes in microporosity are the most difficult to describe accurately. The adsorption processes occurring within mesopores are more easily understood. Macroporosity accounts for less than 1% of the adsorption processes within microporous carbon.

Thermodynamic system of the adsorption is simply that various compounds strive for equilibrium. The process of adsorption occurs in both steady-state and unsteady-state conditions. The primary force driving the interaction between the adsorbate and the adsorbent is the electrostatic attraction and repulsion between molecules of the adsorbate and the adsorbent. These driving forces can be either physical or chemical. In discussing the fundamentals of adsorption, it is useful to distinguish between physical adsorption, involved only relatively weak intermolecular forces, and chemical adsorption, which involve essentially the formation of a chemical bond between the sorbate molecule and the surface of the adsorbent. Table 2.6 shows some differences between physical adsorption and chemical adsorption.

2.4.1 Physical adsorption

Physical adsorption 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 a lower combined free energy. Dispersing interactions are the result of attractive forces between electrons and nuclei of molecular systems. If the molecules come too close to each other, repulsive forces can push the molecules 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 adsorption. Physical adsorption 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 93 kJ/kg per mole of the adsorbate. When the intermolecular forces between a chemical molecule in a liquid stream and a solid (the adsorbent) are greater than the forces between the molecules of the liquid stream, the chemical is adsorbed onto the adsorbent surface.

2.4.2 Chemical adsorption

Chemical adsorption, like physical adsorption, is also based upon electrostatic force. 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 produces 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 186 to 930 kJ/kg per mole. It is not unusual for the adsorbate to have chemical change 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 2.4 Distinction between physical adsorption and chemical adsorption

Physical adsorption	Chemical adsorption
Dipole-dipole interactions, dispersing interactions, and hydrogen bonding	Formation of chemical bonds
Low heat of adsorption (<2 or 3 times latent heat of evaporation)	High heat of adsorption (>2 or 3 times latent heat of evaporation)
Non specific	Highly specific
Monolayer or multilayer	Monolayer only
No dissociation of adsorbed species	May involve dissociation
Only significant at relatively low temperatures	Possible over a wide range of temperatures
Rapid, non-activated, reversible	Activated, may be slow and irreversible
No electron transfer although polarization of sorbate may occur	Electron transfer leading to bond formation between sorbate and surface

2.4.3 Adsorption kinetics

Quantifying the changes in sorption with time requires that an appropriate kinetic model is used. Lagergren's kinetic equation [16] has been most widely used to describe the solute adsorption on various adsorbents. The first-order Lagergren expression based on the solid capacity is

$$\frac{dq}{dt} = k_1(q_e - q) \tag{2.1}$$

where q_e and q are the amount of adsorbed adsorbate on the adsorbent at the equilibrium and at time t, respectively (mmol g^{-1}), and k_1 is the rate constant of first-order adsorption (min^{-1}). After integrating and applying boundary condition, t=0–t=t and q=0- q= q; the integrated form of Eq. (2.1) becomes

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303} t \tag{2.2}$$

A pseudo second-order rate expression based on sorption equilibrium capacity was derived by Ho and McKay [17]. The sorption capacity is assumed to be proportional to the number of active sites occupied on the adsorbent, or

$$\frac{dq}{dt} = k_1(q_e - q)^2 \tag{2.3}$$

Where k_2 are the second-order rate constant with a unit of g $mmol^{-1}min^{-1}$. After integrating and applying boundary condition, t=0-t=t and q=0-q=q; Eq. (2.3) becomes

$$\frac{1}{q_e - q} = \frac{1}{q_e} + k_2 t \tag{2.4}$$

Eq. (2.4) can be rearranged to the linear form as follows;

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{2.5}$$

2.4.4 Adsorption isotherms

Adsorption in a solid-liquid system results in the removal of solute from solution and their concentration at the surface of the solid, to such time as the concentration of the solute remaining in solution is in a dynamic equilibrium with that at the surface. At this position of equilibrium, there is a defined distribution of solute between the liquid and solid phases. This distribution expresses the quantity q_e as a function of C at fixed temperature, the quantity q_e being the amount of solute adsorbed per unit weight of solid adsorbent, and C the concentration of solute remaining in solution at equilibrium. An expression of this type is termed an adsorption isotherm.

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

2.4.4.1 Langmuir isotherm

The Langmuir adsorption model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, that the energy of adsorption is constant, and that there is no transmigration of adsorbate in the plane of the surface. The Langmuir isotherm is

$$\frac{C_e}{q_e} = \frac{C_e}{q_0} + \frac{1}{bq_0} \qquad (2.6)$$

where C_e= the equilibrium concentration of adsorbate in solution (mg/L)
q_e= the amount of the adsorbed adsorbate per unit weight of adsorbent at equilibrium (mg/g)
q_0= the maximum solute concentration in the adsorbent (mg/g)
b= the constant related to the free energy of adsorption

2.4.4.2 Freundlich isotherm

The Freundlich isotherm is a special case for heterogeneous surface adsorption where a multilayer adsorption could occur. The Freundlich isotherm is

$$q_e=K_F C_e^{1/n} \qquad (2.7)$$

where K_F and n are constants, and $n>1$. The Freundlich isotherm is usually fitted to the logarithmic form

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad (2.8)$$

Eq. (2.8) gives a straight line with a slope of $1/n$ and intercept equal to the value of log K_F. The intercept is roughly an indicator of adsorption capacity and the slope, $1/n$, of adsorption intensity.

2.5 Desorption

Desorption is necessary as a means to recover the spent adsorbents, particularly those expensive, high efficiency types. The desorption or regeneration can be accomplished by washing the adsorbent with an appropriate solution. The type, strength and quantity of the desorbing solution must be determined and optimized. Screening for the most effective regenerating solution is imperative, and most often, cationic species are generally released by a simple mild acidic wash.

2.5.1 Desorption kinetics

The pseudo first order expression:

$$-\frac{dq}{dt} = k_{d,1}(q - q_e) \tag{2.9}$$

where q_e and q are the amount of adsorbate on the adsorbent at the equilibrium and at time t, respectively (mg/g), and $k_{d,1}$ is the rate constant of first-order desorption (min^{-1}). After integrating and applying boundary condition, t=0 to t=t and q=q_0 to q=q; Eq. (2.9) becomes

$$\log(q - q_e) = \log(q_0 - q_e) - k_{d,1}t \tag{2.10}$$

The pseudo second order expression:

$$-\frac{dq}{dt} = k_{d.2}(q - q_e)^2 \tag{2.11}$$

where $k_{d,2}$ is the second-order rate constant with a unit of g mmol^{-1} min^{-1}. After integrating and applying boundary condition, t=0-t=t and q=q_0-q=q; Eq. (2.11) becomes

$$\frac{1}{(q - q_e)} - \frac{1}{(q_0 - q_e)} = k_{d,2}t \tag{2.12}$$

2.6 Literature review

2.6.1 Adsorption of organic compound on activated carbon

Franz *et al.* [18] studied the effects of oxygen-containing groups, particularly carboxylic and carbonyl groups, on the adsorption of dissolved aromatics on activated carbon. The results showed that water adsorption, dispersive/repulsive interactions, and hydrogen-bonding were the main mechanisms by which surface oxygen groups influence the adsorption capacity, while donor-acceptor interactions were found not to be significant. The adsorption mechanism was also found to be influenced by the properties of the functional group on the aromatic adsorbate, especially its ability to hydrogen-bond and through its activating/deactivating influence on the aromatic ring.

Hameed *et al.* [19] studied the adsorption characteristics of 2,4,6-trichlorophenol on coconut husk-based activated carbon. The results showed that adsorption capacity increased with increasing in initial concentration and agitation time, while acidic pH was more favorable for the adsorption of 2,4,6-trichlorophenol. The equilibrium data were best represented by the Langmuir isotherm, yielding maximum monolayer adsorption capacity of 716.10 mg/g at 30^{o}C. The adsorption kinetics was found to follow the pseudo-second-order kinetic model.

Chen *et al*. [20] studied granular activated carbon for removal of organic compounds in drinking water. The results showed that the better adsorption efficiency of granular activated carbon was in the higher initial concentration of total organic carbon from the drinking water source. The adsorption capability and the Freundlich constant increased with increasing operation time.

Tomaszewska *et al*. [21] studied the removal of organic matter by coagulation enhanced with adsorption on powdered activated carbon. The study showed that coagulation without powdered activated carbon addition was less effective than the adsorption-coagulation integrated system. Coagulation enhanced with adsorption on activated carbon was more effective when coagulation was preceded by adsorption than when the two processes were carried out simultaneously. Small molecules were preferentially adsorbed from mixtures (such as a mixture of phenol and humic acids). Phenol occupies the active sites of powdered activated carbon faster than humic acids. The decrease in K_F values was about 30% when humic acids were in mixture with phenol.

Ayranci and Duman [22] studied the adsorption of aromatic organic acids onto high area activated carbon cloth in relation to wastewater purification. The results showed that adsorption of aromatic organic acids, benzoic acid, salicylic acid, nicotinic acid and *p*-aminobenzoic acid onto high area activated carbon cloth from solutions in 0.4 M H_2SO_4, in water, in 0.1 M NaOH and from solutions at pH 7.0 followed the first-order kinetics. The rate and extent of adsorption of all four compounds were the highest in water or in 0.4 M H_2SO_4 solutions and the lowest in 0.1 M NaOH solution.

2.6.2 Adsorption of salicylic acid and humic acids on adsorbent

Thomas *et al*. [23] studied the adsorption of salicylate and polyacrylate on mesoporous alumina. The results showed that salicylic acid is preferentially adsorbed on the walls of the mesopores with no effect on the charge of the external surface. When adsorption inside the pores was complete, it spreaded over the external surface causing a decrease of the zeta potential.

Ngah *et al*. [24] studied the adsorption of humic acids on crosslinked chitosan-epichlorohydrin beads. The study showed that optimum humic acids adsorption on crosslinked chitosan-epichlorohydrin beads occurred at pH 6.0, agitation rate of 300 rpm and contact time of 50 min. Freundlich model was found to show the best fit for experimental data while the maximum adsorption capacity determined from Langmuir model was 44.84 mg/g. The adsorption of humic acids on crosslinked chitosan-epichlorohydrin beads was best described with pseudo-first-order kinetic model.

Anirudhan *et al*. [25] studied the adsorption of humic acids on amine-modified polyacrylamide-bentonite composite. The pH dependent sorption of humic acids was found maximum at pH range 4.0-7.0 for an initial concentration of 25 µmol/L. The removal mechanism of humic acids by amine-modified polyacrylamide-bentonite composite was mainly through the complexation of the carboxyl groups in humic acids with the protonated NH_2 group in amine-modified polyacrylamide-bentonite composite. The kinetics of adsorption follows pseudo-second-order model. The equilibrium conditions were achieved within 3 hours. The equilibrium data were well fitted to Langmuir isotherm. The monolayer adsorption capacity was 103.91 µmol/g at 30°C.

Wang and Zhu [26] studied humic acids adsorption on fly ash. The results showed that metal oxides and unburned carbon in fly ash exhibited significant difference in humic acids adsorption. The unburned carbon plays the major role in adsorption. Higher content of unburned carbon in fly ash results in higher surface area and thus higher humic acids adsorption. Fly ash and unburned carbon exhibited adsorption capacity of humic acids of 11 and 72 mg/g, respectively, at 30°C, pH 7.

Imyim and Prapalimrungsi [27] studied humic acids removal from water by aminopropyl functionalized rice husk ash. The study showed that optimum conditions for humic acids adsorption on modified rice husk ash were found to be 30 min equilibrium time and initial pH in the range of 3-4. Experimental adsorption data fitted well with the Langmuir equation and the maximum adsorption capacity was 8.2 mg/g at pH 6.

2.6.3 Regeneration of activated carbon

Ania *et al*. [28] studied the application of microwaves for the regeneration of activated carbons spent with salicylic acid, a metabolite of a common analgesic frequently found in wastewater from the pharmaceutical industry. The exhausted carbon was treated in a quartz reactor by microwave irradiation at 2450 MHz at different temperatures and atmospheres. Result showed that quantitative desorption of the pollutant was achieved at high temperature and oxidizing atmosphere, with regeneration efficiencies as high as 99% after six cycles.

Castilla *et al*. [29] studied the thermal desorption process of phenol, *m*-aminophenol, *p*-cresol and *p*-nitrophenol from an activated carbon. The activated carbon-phenolic compound system was heated to 1100 K in a He flow. Result showed that during the adsorption process of the phenolic compounds on activated carbons from aqueous solutions, this is physisorption and chemisorption. When this activated carbon-phenolic compound system was heat-treated up to 1100 K in an inert gas flow, the physisorbed phenol evolved at a low temperature from the surface of the carbon and is deposited at the outlet of the reactor. The capacity of activated carbon to adsorb phenolic compounds decreased as the number of adsorption-regeneration cycle increase. The extent of this decrease depends on the phenol type.

Lim and Okada [30] studied the regeneration of granula activated carbon using ultrasound. The result showed that about 64% of trichloroethylene was desorbed from 5 g of granular activated carbon loaded with 6.5 mg trichloroethylene for 1 hour in ultrasonic field at 20 kHz and trichloroethylene desorbed to liquid phase were rapidly degraded by ultrasound.

Zhang [31] studied the regeneration of exhausted activated carbon by electrochemical method. The result showed that the electrochemical method could be used to regenerate the activated carbon exhausted with phenol. The electrochemical regeneration efficiency can reach 85.2% in stirred electrochemical reactor regeneration for 5 hours.

Based on the literature survey, it can be concluded that activated carbon could be used for the removal of humic substances. The adsorption study of salicylic acid and humic acids has been discussed in many works, nevertheless, the study of simultaneous adsorption of salicylic and humic acids on granular activated carbon has not been discussed before. Moreover, the regeneration of granular activated carbon has normally employed strong conditions such as temperature at 1100 K [29] or complicated instrument such as microwave [28], ultrasound [30] and electrochemical method [31]. The aim of this work was to study of simultaneous adsorption of salicylic acid and humic acids on granular activated carbon under optimal conditions and study of regeneration of granular activated carbon by elution with suitable eluent under suitable condition.

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 salicylic acid and humic acids at wavelength of 308 and 254 nm, respectively.

3.1.2 pH meter

A pH meter model Orion Star Series (Thermo Electron Corporation) was used for pH measurements.

3.1.3 Shaker

A shaker model HS 500 (Janke&Kunkel) was used for shaking of salicylic acid and humic acids solutions.

3.2 Chemicals

All chemicals were standard analytical grade as listed in Table 3.1

Table 3.1 Chemicals lists

Chemicals	Supplier
Granular activated carbon (20-60 mesh, 600 m^2/g)	Sigma
Salicylic acid	Merck
Humic acid sodium salt (87.6%)	Aldrich
Ethanol	Merck
Sodium hydroxide	Merck
Hydrochloric acid	Merck

3.3 Methodology

3.3.1 Humic acids purification

10 g of humic acids (sodium salt) were dissolved in 1 L of NaOH solution with pH 11.0, the suspended solution was stirred overnight and then centrifuged to remove undissolved matters. To precipitate humic acids fraction, the supernatant solution was brought to pH 2.0 with 1 M HCl, stirred for 24 hours and centrifuged. The precipitate was rinsed with 0.01 M HCl several times to bring the humic acids in its protonated form and to remove soluble fractions and inorganic salts. The humic acids were dried at 110^{o}C for 24 hours for further use.

3.3.2 Determination of pH of point of zero charge of granular activated carbon by mass titration technique

Different masses of granular activated carbon within the concentration range of 5-100 g/L were put into contact with a 0.03 M KNO_3 solution. The aqueous suspentions were shaken for 24 hours until the equilibrium pH was reached. The pH of point of zero carge (pH_{PZC}) is the pH at which a plateau is achieved when plotting equilibrium pH versus sorbent mass [32].

3.3.3 Preparation of chemicals

All solutions were prepared using de-ionized water.

3.3.3.1 Salicylic acid solutions

A stock standard solution (1000 mg/L) of salicylic acid was prepared by dissolving 1.0 g of salicylic acid in 1 L of 0.1 M NaOH solution. Working standard solutions were prepared by dilution of 1000 mg/L salicylic acid standard solution to required concentrations.

3.3.3.2 Humic acids solutions

A stock standard solution of humic acids was prepared by dissolving 0.2 g of purified humic acids in 1 L of 0.1 M NaOH solution, the mixture was stirred for 48 hours and then filtered through filter papers (Whatman No.1). Working standard solutions were prepared by dilution of 200 mg/L humic acid standard solution to required concentrations.

3.3.3.3 Eluent solutions

5 %(w/v) NaOH solution was prepared by dissolving the appropriate amount of NaOH in deionized water.

5 %(w/v) NaOH in 10 % (v/v) ethanol/water, 10 %(w/v) NaOH in 10 %(v/v) ethanol/water and 10 %(w/v) NaOH in 60 %(v/v) ethanol/water were prepared by dissolving the appropriate amount of NaOH in ethanol/water solutions.

3.4 Adsorption study

3.4.1 Effect of initial pH of solutions

Salicylic acid solutions were prepared by dilution of 1000 mg/L salicylic acid stock solution in de-ionized water and the final concentration was 100 mg/L. Initial pH of the solutions was adjusted in the range of 1.0 to 10.0. The pH values were adjusted by adding 1% hydrochloric acid and 1% sodium hydroxide solutions. In all cases, 10 mL of salicylic acid solution was contacted with 10 mg granular activated carbon and shaken for 60 min. The solutions were filtered and analyzed for the remaining salicylic acid concentration by UV-Vis method.

Humic acid solutions were prepared by dilution of 200 mg/L humic acid stock solution in de-ionized water and the final concentration was 50 mg/L. Initial pH of the solution was adjusted in the range of 4.0 to 10.0. The adsorption study was performed by the same manner of salicylic acid.

3.4.2 Effect of initial concentration

Salicylic acid solutions were prepared by dilution of 1,000 mg/L salicylic acid stock solution in de-ionized water and the final concentrations were varied between 100-700 mg/L. 10 mL of salicylic acid solution was contacted with 10 mg granular activated carbon by shaking for 6 hours. The solutions were filtered and analyzed for the remaining salicylic acid concentration by UV-Vis method.

Humic acids solutions were prepared by dilution of 200 mg/L humic acid stock solution in de-ionized water and the final concentrations were varied between 10-100 mg/L. The adsorption study was performed by the same manner of salicylic acid.

3.4.3 Effect of contact time

Salicylic acid and humic acids solutions were prepared by dilution of the stock solution in de-ionized water to an optimal concentration. 10 mL of solution was contacted with 10 mg granular activated carbon by shaking for 10-360 min. The solutions were filtered and analyzed for the remaining acids concentration by UV-Vis method.

3.4.4 Simultaneous adsorption

Stock salicylic acid solution and humic acids solution were mixed. The mixture solution was adjusted to pH 4.0 and the final concentrations of salicylic acid and humic acids were 400 and 100 mg/L, respectively. 10 mL of the mixture solution was contacted with 10 mg granular activated carbon by shaking at an optimal contact time. The solutions were filtered and analyzed for the remaining salicylic acid and humic acid concentrations by UV-Vis method.

3.5 Desorption study

3.5.1 Effect of eluent type

All experiments were carried out by shaking 10 mL of salicylic acid and humic acids solution with 10 mg granular activated carbon under optimal adsorption conditions, consequently, the solutions were filtered and analyzed for the remaining salicylic acid and humic acids concentration by UV-Vis method. The sorbent was washed with de-ionized water and eluted with 10 mL of various eluents (i.e. absolute ethanol, 5 %(w/v) NaOH, 5 %(w/v) NaOH in 10 %(v/v) ethanol/water, 10 %(w/v) NaOH in 10 %(v/v) ethanol/water, 10 %(w/v) NaOH in 60 %(v/v) ethanol/water) for 60 min. The solutions were filtered and analyzed for the released salicylic acid and humic acids concentration by UV-Vis method.

3.5.2 Effect of elution time

All experiments were carried out by shaking 10 mL of salicylic acid and humic acids solution with 10 mg granular activated carbon under the optimal adsorption conditions, the solutions were filtered and analyzed for the remaining salicylic acid and humic acids concentrations by UV-Vis method. The sorbent was washed with de-ionized water and eluted with 10 mL of selected eluent for 10 to 180 min. The solutions were filtered and analyzed for the released salicylic acid and humic acids concentration by UV-Vis method.

3.6 Column method

10 mg of granular activated carbon was packed in a homemade mini-column (I.D. 3 mm, length 15 mm, PVC). The pH of salicylic acid and humic acids solutions were adjusted to pH 1.0 and 4.0, respectively. 10 mL of 400 mg/L salicylic acid solution were passed through the column at a flow rate of 0.5 mL/min. The sorbed acid was desorbed by passing 10 mL of NaOH, 5 %(w/v) NaOH in 10 %(v/v) ethanol/water at a flow rate 0.5 mL/min. The salicylic acid concentration in eluent was determined by UV-Vis method.

10 mL of 100 mg/L humic acids solution were passed through the column at a flow rate of 0.5 mL/min. The sorbed acid was desorbed by passing 10 mL of NaOH, 5 %(w/v) NaOH in 10 %(v/v) ethanol/water at a flow rate 0.5 mL/min. The humic acids concentration in eluent was determined by UV-Vis method.

3.7 Regeneration study

10 mg of granular activated carbon was shaken with 10 mL of the mixture solution under optimal conditions. The solutions were filtered and analyzed for the remaining salicylic acid and humic acids concentrations. The sorbent was washed with de-ionized water and eluted with 10 mL of an appropriate eluent under optimal conditions; the solutions were filtered and analyzed for salicylic acid and humic acids concentrations. The adsorption and desorption onto the sorbent was then repeated for 5 cycles.

CHAPTER IV

RESULTS AND DISCUSSION

The results from the experiments and their analysis for each particular topic are separately presented as follows:

4.1 Point of zero charge determination

The pH at which the sorbent surface charge takes a zero value is defined as the point of zero charge (pH_{PZC}). At this pH, the charge of the positive surface sites is equal to that of the negative one. The pH_{PZC} is the pH at which a plateau is achieved when plotting equilibrium pH versus sorbent mass. As shown in Figure 4.1, the pH_{PZC} obtained by using the mass titration technique was 9.8. The pH_{PZC} was used to describe effect of initial pH of solution. In solutions with pH < $pH_{PZC,}$ the activated carbon surface is positively charged, in solutions with pH > $pH_{PZC,}$ the activated carbon surface is negatively charged.

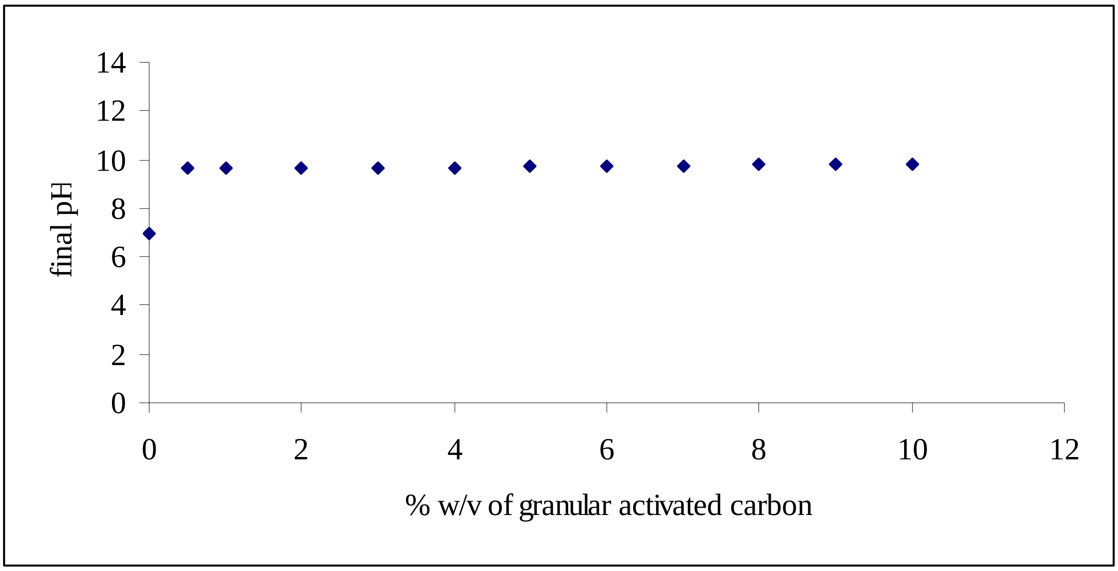

Figure 4.1 Experimental mass titration curve of granular activated carbon.

4.2 Adsorption study

The adsorbed amount of adsorbate per gram of sorbent, *q* (mg/g), was calculated from Eq. 4.1.

$$q = \frac{(C_0 - C)V}{w} \qquad (4.1)$$

where C_0 is the initial adsorbate concentration (mg/L), C is the final adsorbate concentration (mg/L), V is the volume of the adsorbate solution (L), and w is the weight of the adsorbent (g).

4.2.1 Effect of initial pH of solutions

In this experiment, we assumed that the adsorption kinetics of the sorbates at all pH was similar, thus the contact time was fixed at 60 min for all experimental acquisition. It was true that the adsorption equilibrium has not reached yet, however the equilibrium contact time would be investigated in the section 4.2.4.

As shown in Figure 4.2, the adsorption amount of salicylic acid decreased with increasing pH.

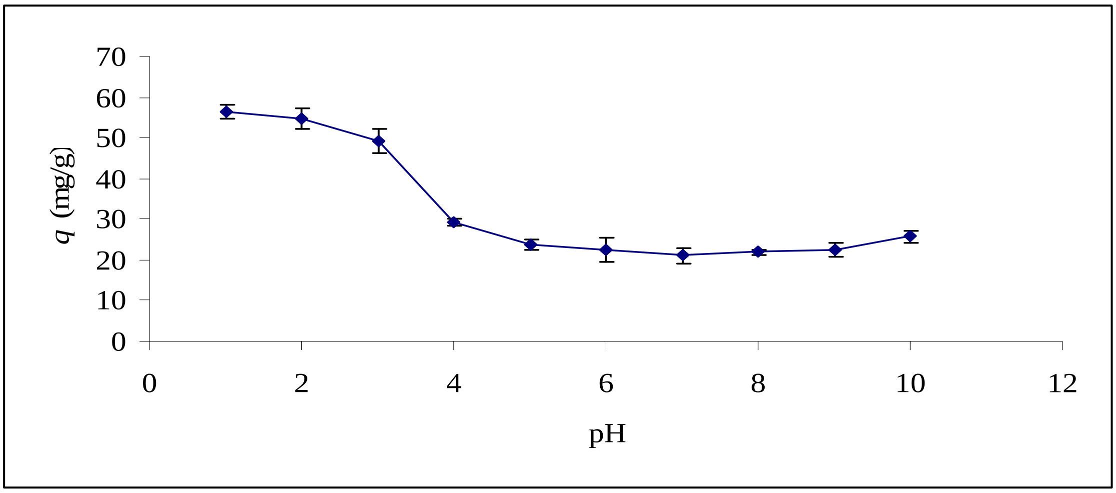

Figure 4.2 Effect of pH of salicylic acid solution; salicylic acid concentration = 100 mg/L, volume = 10 mL, granular activated carbon = 10 mg, contact time = 60 min.

In solutions with pH <3.0, the activated carbon surface is positively charged since the pH values of these solutions are much less than pH_{PZC}, salicylic acid is in more neutral molecular form as the pH values of these solutions are less than pK_a (Figure 4.3). Here, the dispersion interactions and to a certain extent the electrostatic interactions between positively charged surface and either the ¶-electrons of the aromatic ring or the dipole of the adsorbate are expected to be effective in the resulting high rate of adsorption.

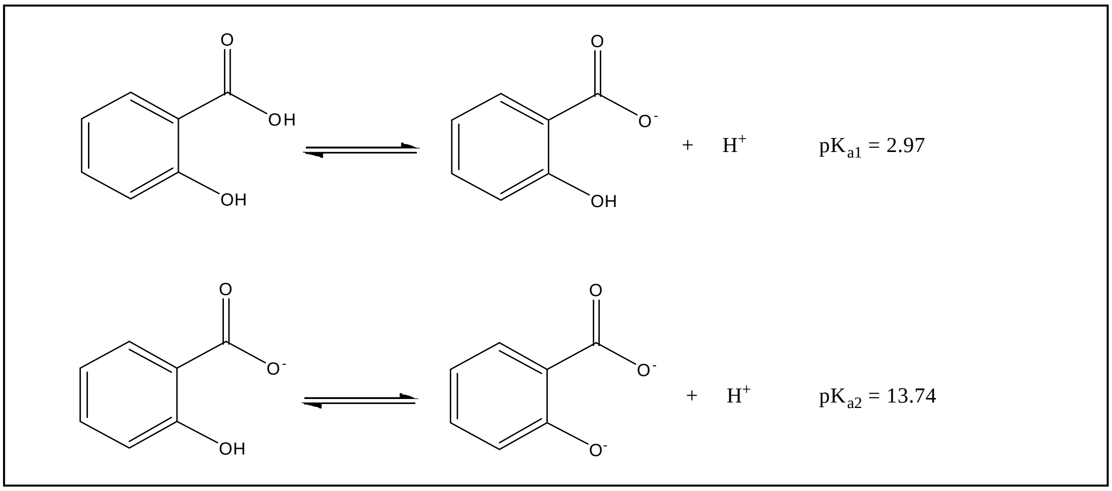

Figure 4.3 Dissociation of salicylic acid.

In solutions at pH 3.0-9.0, the activated carbon surface is positively charged since the pH values of these solutions are less than pH_{PZC}, salicylic acid is more negatively charged form as the pH values of these solutions are more than pK_a. Nonetheless, the dispersion interactions and electrostatic interactions between positively charged surface and negatively charged salicylic molecule are effective in adsorption of salicylic acid on sorbent. On the other hands, salicylic acid is more dissociated at pH of these solutions which lead to high solubility. Therefore, the adsorption of salicylic acid at pH of these solutions is less than in solution at pH <3.0.

In solutions at pH 10, the activated carbon surface is negatively charged since the pH values of these solutions are greater than pH_{PZC} and salicylic acid is negatively charged. Considering these charges and electrostatic repulsion, it is understandable to observe the least adsorption in basic solutions, because the adsorbent surface and salicylic acid are of the same negative charge. The small amounts of adsorptions observed in solutions at pH 10 are expected to result from dispersion interactions.

All of these results correspond to the reported data by Ayranci and Duman [33]. They studied adsorption of aromatic organic acids on activated carbon cloth. The results showed that in 0.4 M H_2SO_4 solutions, the adsorption of aromatic organic acids were higher than in solutions at pH 7.0. In 0.1 M NaOH solutions, the adsorption of aromatic organic acids was smallest.

As shown in Figure 4.4, the adsorption of humic acids on granular activated carbon increased when initial pH decreased. This can be explained by considering humic acids solution as mixtures of compounds with weakly acidic functional groups such as carboxylic, phenolic, carbonyl and hydroxyl [6]. At lower pH, more of these groups are in an uncharged state. Therefore, it is expected that less hydrophilic part of the humic polymer would bind hydrophobic compounds more effectively. Similar pH effect on humic acids adsorption had been reported during the adsorption of humic acids on other adsorbents such as fly ash [26], clay [34], and chitosan [35].

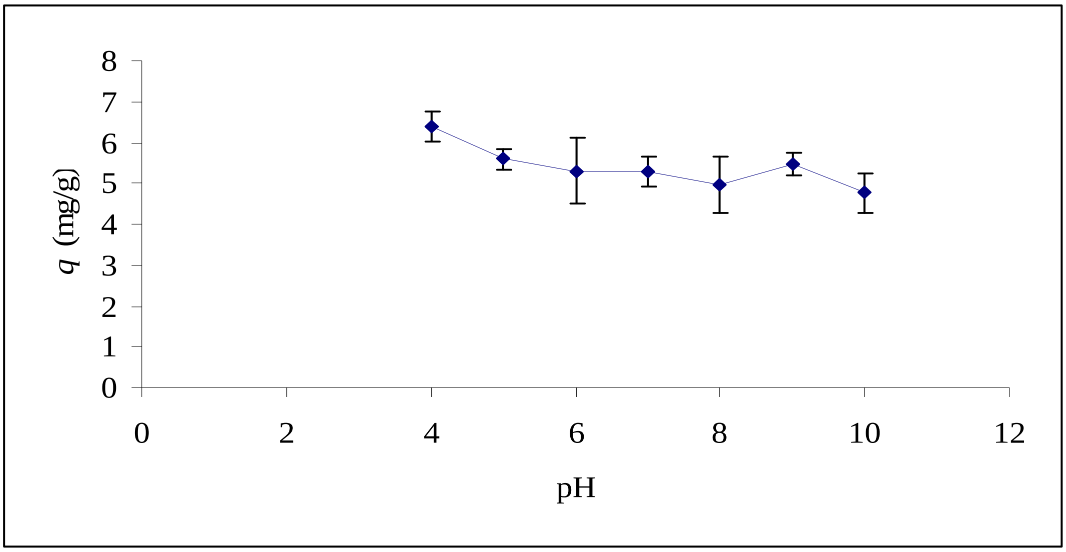

Figure 4.4 Effect of pH of humic acids solution; Humic acids concentration = 50 mg/L, volume = 10 mL, granular activated carbon = 10 mg, contact time = 60 min.

The initial pH of humic acids solution was studied at pH range 4.0 – 10.0 due to the humic acids start to precipitation at pH < 3.0.

In solutions at pH <5.0, the carbon surface is positively charged since the pH values of these solutions are much less than pH_{PZC}, humic acids are more neutral molecular form since the pH values of these solutions are less than pK_a (5.81-5.99) [36], which shown in Eq. 4.2. Here, the dispersion interactions and to a certain extent the electrostatic interactions between positively charged surface and either the ¶-electrons of the aromatic ring or the dipole of the adsorbate are expected to be effective in the resulting high rate of adsorption.

$$\text{HA-COOH} \longrightarrow \text{HA-COO}^- + H^+ \qquad pK_a = 5.81\text{-}5.99 \qquad (4.2)$$

$$\text{HA-OH} \longrightarrow \text{HA-O}^- + H^+ \qquad pK_a = 9.30\text{-}9.52 \qquad (4.3)$$

where HA-COOH represents a humic acids carboxylic group, HA-OH represents a humic acids phenolic group.

In solutions at pH 6.0-9.8, the carbon surface is positively charged since the pH values of these solutions are less than pH_{PZC} and humic acids are negatively charged due to the carboxylic groups start to dissociate their proton at pH 5.81-5.99. Nonetheless, the dispersion interactions and electrostatic interactions between positively charged surface and negatively charged of humic molecule are effective in adsorption of humic acids on sorbent. On the other hands, humic acids are more dissociate at pH of these solutions and lead to high solubility. Therefore, the adsorption of humic acids at pH of these solutions is less than in solution at pH <5.0.

In solutions at pH >9.8, the carbon surface is negatively charged since the pH values of these solutions are greater than pH_{PZC} and humic acids are more negatively charged due to the phenolic groups start to dissociate their proton at pH 9.30-9.52 [36], which shown in Eq. 4.3. Therefore, the adsorption of humic acids in solutions at pH >9.0 is lower than all of the results at lower pH.

To achieve high adsorption capacity, pH 1.0 of salicylic acid solution and pH 4.0 of humic acids solution were selected for subsequent works.

4.2.2 Effect of initial concentration

As shown in Figure 4.5, the capacity of salicylic acid adsorption increased with rising initial concentration of the solute up to 400 mg/L. Above this concentration no further rise was observed probably due to the limited active sites available to adsorb salicylic acid on the granular activated carbon. As shown in Figure 4.6, the capacity of humic acid adsorption increased with rising initial concentration of the solute up to 100 mg/L. Above this concentration, the experiment could not be performed because the precipitation of humic acids occurred.

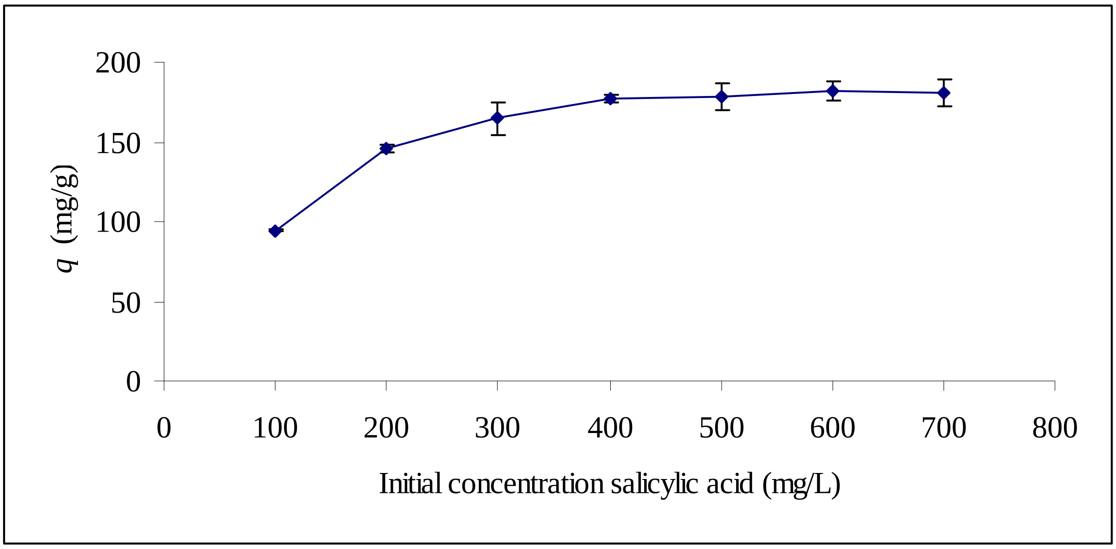

Figure 4.5 Effect of initial concentration of salicylic acid; pH =1, volume = 10 mL, granular activated carbon = 10 mg, contact time = 360 min.

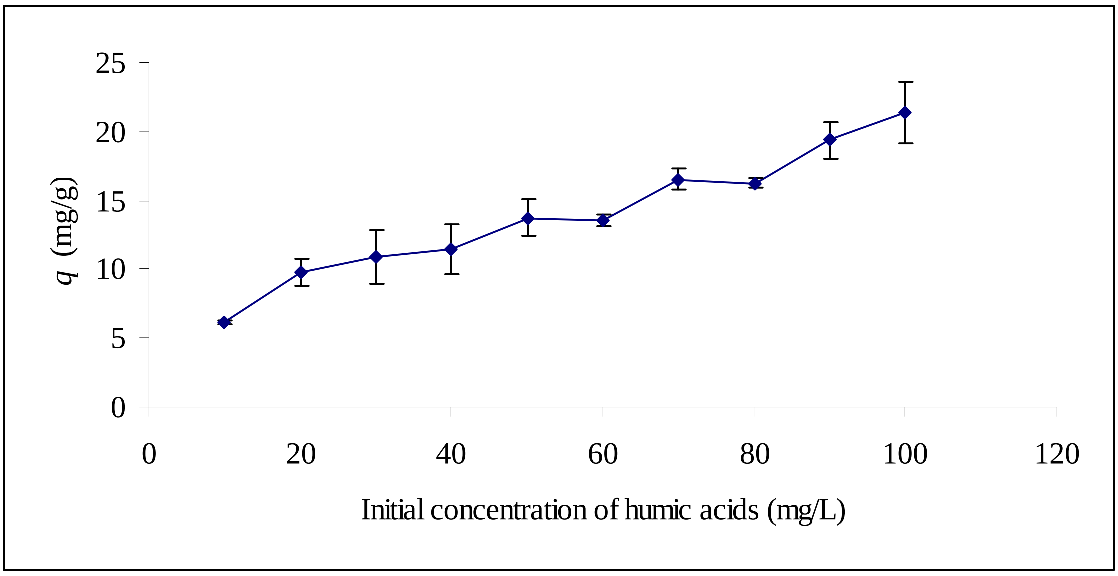

Figure 4.6 Effect of initial concentration of humic acid; pH = 4, volume = 10 mL, granular activated carbon = 10 mg, contact time = 360 min.

4.2.3 Adsorption isotherms

The adsorption isotherm studies were carried out based on two isotherm models, the Langmuir isotherm and the Freundlich isotherm. The Langmuir isotherm model [37] is represented by Eq. 4.4.

$$\frac{C_e}{q_e} = \frac{C_e}{q_0} + \frac{1}{bq_0} \qquad (2.6)$$

where C_e= the equilibrium concentration of adsorbate in solution (mg/L)
q_e= the amount of the adsorbed adsorbate per unit weight of adsorbent at equilibrium (mg/g)
q_0= the maximum solute concentration in the adsorbent (mg/g)
b= the constant related to the free energy of adsorption

The Freundlich isotherm model [38] is represented by Eq. 4.5.

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad (2.8)$$

where C_e= the equilibrium concentration of adsorbate in solution (mg/L)
q_e= the amount of the adsorbed adsorbate per unit weight of adsorbent at equilibrium (mg/g)
K_F= Freundlich's constant related to the sorption capacity
n= Freundlich's constant related to the sorption intensity of an adsorbent

Table 4.1 Langmuir and Freundlich constants adsorption of salicylic acid and humic acids onto granular activated carbon

Adsorbate	Langmuir isotherm			Freundlich isotherm		
	q_0 (mg/g)	b (L/mg)	R^2	K_F	$1/n$	R^2
Salicylic acid	185.19	0.091	0.9996	76.68	0.147	0.9586
Humic acids	25.64	0.031	0.8919	2.65	0.440	0.9576

The Langmuir adsorption isotherm of salicylic acid was shown in Figure 4.7. A straight line was obtained by plotting of C_e/q_e against C_e (R^2>0.99). This indicates that the adsorption of salicylic acid onto granular activated carbon is fitted by means of the Langmuir isotherm. The adsorption isotherm indicates that the adsorption of salicylic acid on granular activated carbon is monolayer. This result corresponds to the report of Otero *et al.* [39]. As shown in Table 4.1, the Langmuir constant (b) calculated from the linear equation is 0.091 L/mg. The maximum adsorption capacity (q_0) from the calculation is 185.19 mg/g with monolayer coverage of salicylic acid onto the adsorbent.

As shown in Figure 4.8, a less linear relation was obtained by plotting the data of humic acids (R^2<0.97). This indicates that the adsorption of humic acids onto granular activated carbon is less fitted by means of the Langmuir isotherm than that of salicylic acid. The maximum adsorption capacity (25.64 mg/g) and the Langmuir constant (0.031 L/mg) are much lower than those of salicylic acid. This result suggests that salicylic acid is more favorable upon granular activated carbon monolayer adsorption.

As shown in Table 4.1, the maximum adsorption capacity of salicylic acid onto granular activated carbon from the calculation by Langmuir isotherm is more than that of humic acids. It could be explained that molecular size of salicylic acid is smaller than molecular size of humic acids, resulting that former could adsorb better in small pore of granular activated carbon while humic acids could not.

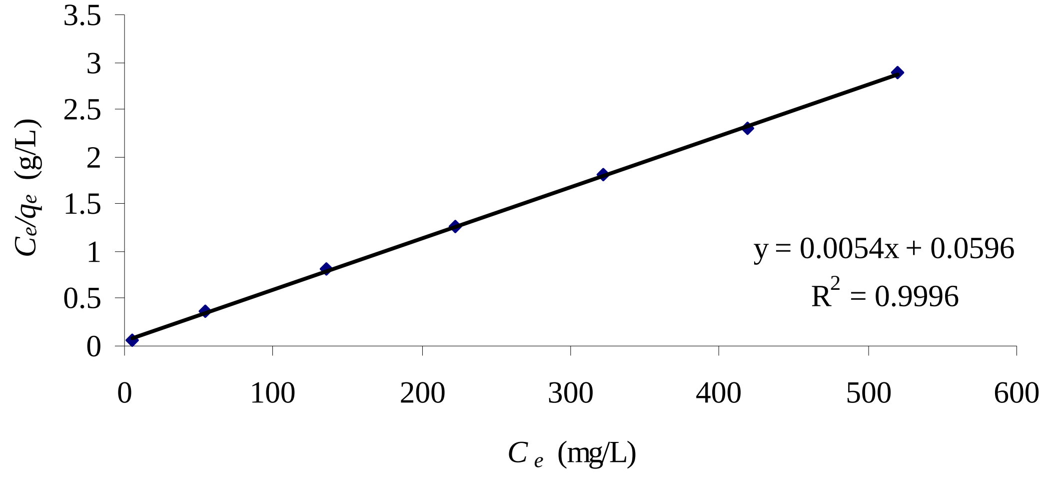

Figure 4.7 Langmuir plot of salicylic acid adsorption by granular activated carbon.

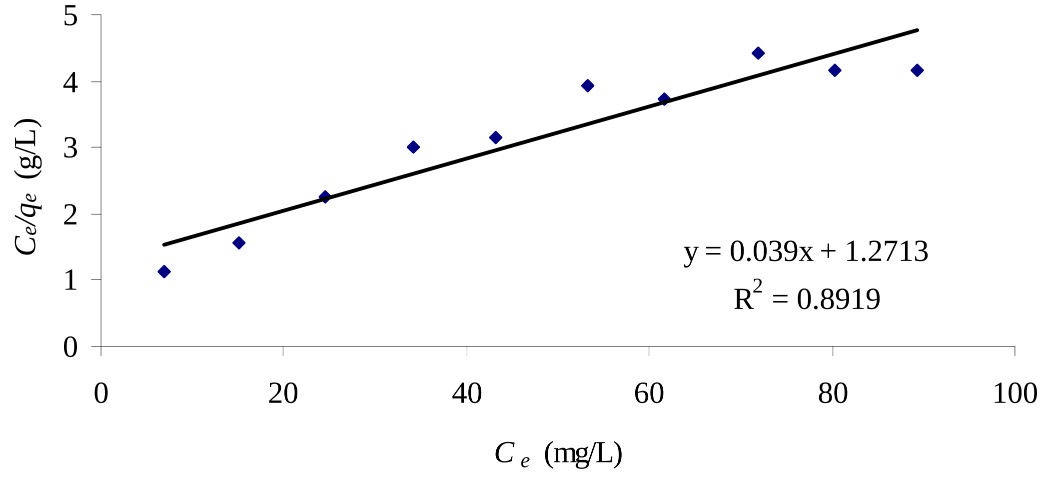

Figure 4.8 Langmuir plot of humic acids adsorption by granular activated carbon.

The adsorption capacities of the adsorbents for the removal of salicylic acid and humic acids have been compared with those of other adsorbents from the literature as shown in Table 4.2 and 4.3, respectively. The values reported are in the form of monolayer adsorption capacity. The experimental data of the present investigations are comparable with nonionic polymer resin and activated carbon from rice husk.

Table 4.2 Adsorption capacity of various adsorbents towards salicylic acid

Adsorbent	Capacity (mg/g)
Filtrasorb F400 (granular activated carbon) [39]	351.1
Sephabeads SP207 (nonionic polymeric resin) [39]	81.6
Sephabeads SP206 (nonionic polymeric resin) [39]	45.2
Duolite S861 (nonionic polymeric resin) [40]	43.01
Amberlite (nonionic polymeric resin) [40]	81.68
Granular activated carbon [this work]	175.4

Table 4.3 Adsorption capacity of various adsorbents towards humic acids

Adsorbent	Capacity (mg/g)	Adsorption conditions	
		Humic acids	pH
Activated carbon from rice husk [41]	21-45	Fluka (sodium salt)	5
Pillared bentonite [34]	537	Aldrich (sodium salt)	4
Chitosan [42]	57.14	Aldrich (sodium salt)	3.5
Goethite [43]	188	Local humic acids	4
Activated sludge [44]	2.4	Aldrich (sodium salt)	4.4
Rice husk ash [27]	2.7	Aldrich (purified)	6.0
Modified rice husk ash [27]	8.2	Aldrich (purified)	6.0
Granular activated carbon [this work]	16.3	Aldrich (purified)	4.0

The Freundlich adsorption isotherm of salicylic acid is shown in Figure 4.9. A less linear relation was obtained by plotting the data of salicylic acid (R^2<0.97). This indicates that the adsorption of salicylic acid onto granular activated carbon is less fitted by means of the Freundlich isotherm.

As shown in Figure 4.10, the plot of log q_e *vs* log C_e of humic acids is linear. This indicates the applicability of Freundlich isotherm, which is consistent with other studies reported on the adsorption of humic acids by powdered activated carbon in saline water condition [45]. As shown in Table 4.1, the slope (1/*n*) of line is 0.440. The adsorption process is favorable when the value of 1/*n* lies between 0.1 and 1. The K_F of humic acids calculated from the intercept of this line is 2.65 mg/g. This result suggests that the adsorption of humic acids prefers multilayer adsorption. As mentioned in section 2.1.2, humic acids have an abundance of aromatic moiety and various functional groups, this may presumably allow self adsorption of humic acids onto other humic acids previously adsorbed on the activated carbon surface (or first monolayer adsorbed humic molecules) due to ¶-¶ interactions of aromatic moieties or p-orbital of N-, O-containing functional groups.

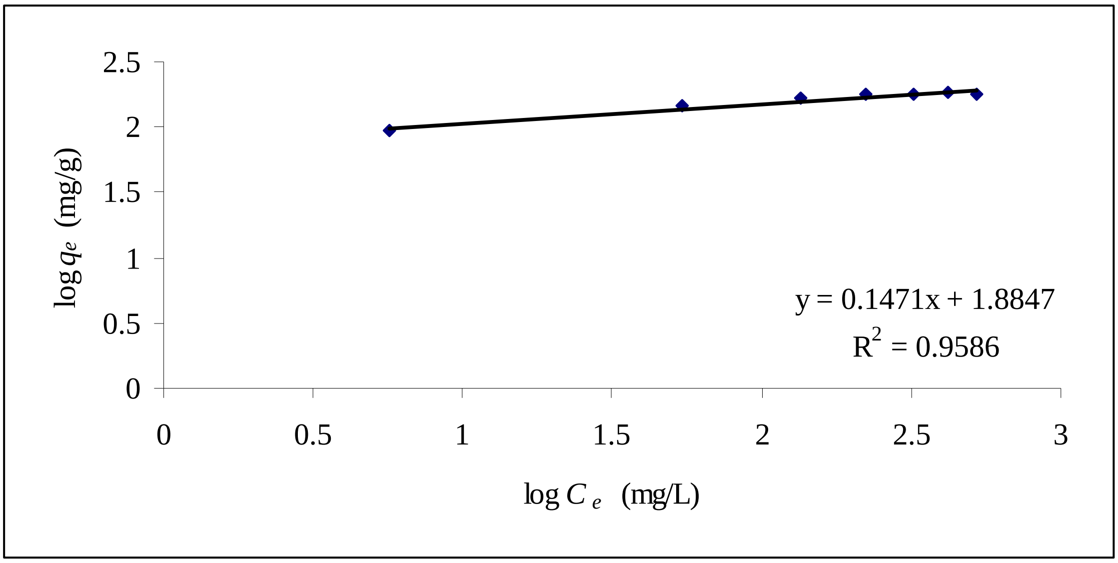

Figure 4.9 Freundlich plot of salicylic acid adsorption by granular activated carbon.

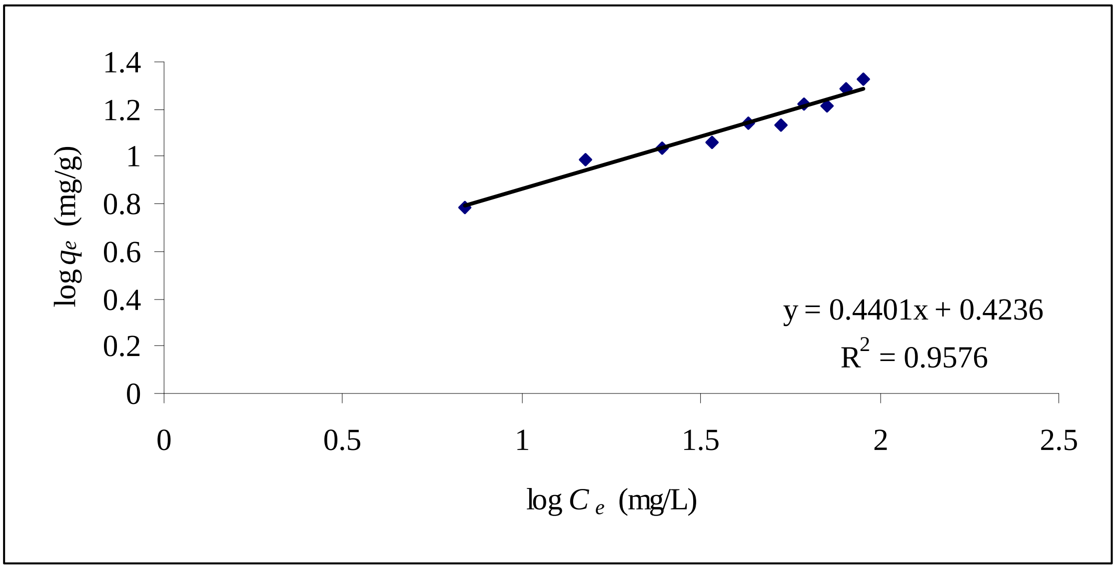

Figure 4.10 Freundlich plot of humic acids adsorption by granular activated carbon.

4.2.4 Effect of contact time

The effect of contact time on salicylic acid adsorption onto granular activated carbon is shown in Figure 4.11. The capacity of salicylic acid adsorption increased in 0.5-2 hours, and then the adsorption rate decreased gradually and reached equilibrium in about 2 hours. As shown in Figure 4.12, the capacity of humic acids adsorption increased in 1-3 hours, and then the adsorption rate decreased and almost reached equilibrium in about 4 hours. To achieve high adsorption capacity, contact time of 4 hours was selected for subsequent works.

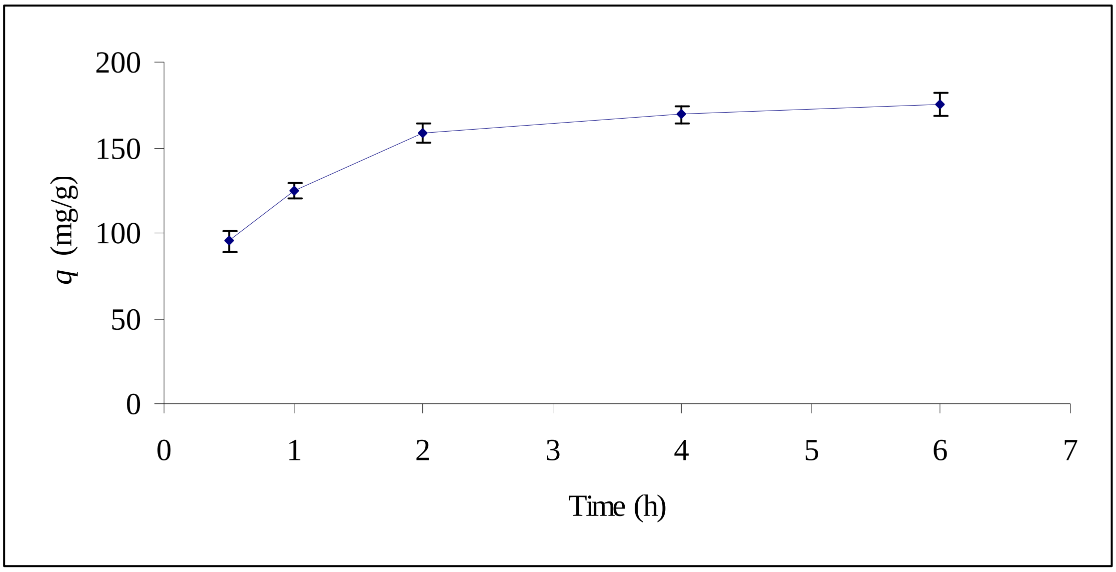

Figure 4.11 Effect of contact time on salicylic acid adsorption; salicylic acid concentration = 400 mg/L, pH = 1, volume = 10 mL, granular activated carbon = 10 mg.

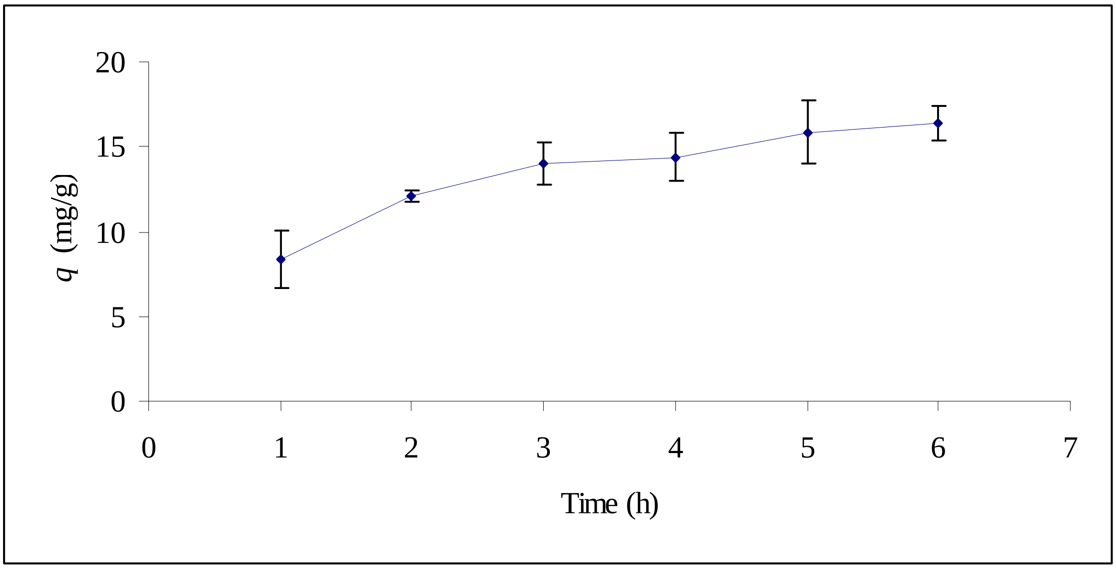

Figure 4.12 Effect of contact time on humic acids adsorption; humic acids concentration = 100 mg/L, pH = 4, volume = 10 mL, granular activated carbon = 10 mg.

4.2.5 Adsorption kinetics

The most commonly used pseudo-first order and pseudo-second order models were employed to explain the solid/liquid adsorption. The pseudo-first order and pseudo-second order kinetic models were used to predict kinetic parameters for the adsorption of salicylic acid and himic acids onto granular activated carbon. The pseudo-first order and pseudo-second order kinetic models are used to quantifying the changes in sorption with time require. The pseudo-first order and pseudo-second order kinetic models are shown in Eqs. (4.6) and (4.7), respectively

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{2.2}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{2.5}$$

where q_t and q_e are the adsorption amounts at certain time and at equilibrium time, respectively, mg/g; k_1 is the pseudo-first order rate constant, min^{-1}; and k_2 is the rate constant of pseudo-second order equation, g/(mg·min).

Table 4.4 Pseudo-first order and pseudo-second order kinetic parameters of salicylic acid and himic acids adsorption onto granular activated carbon

adsorbate	$q_{e,exp}$ (mg/g)	First-order kinetic model			Second-order kinetic model		
		$q_{e,cal}$ (mg/g)	k_1 (min^{-1})	R^2	$q_{e,cal}$ (mg/g)	k_2 (g/mg·min)	R^2
Salicylic acid	175.38	81.56	0.573	0.9500	188.68	0.011	0.9996
Humic acids	16.35	11.33	0.487	0.8364	19.96	0.037	0.9970

The experimental adsorption data of salicylic acid and humic acids onto the granular activated carbon are not fitted with the pseudo-first order kinetic model, as shown in Figure 4.13 and 4.14, but agree with the pseudo-second order kinetic model (R^2>0.99). The result indicated that the initial concentration of salicylic acid and humic acids is effected to the adsorption. The plots of t/q_t vs t for salicylic acid and humic acids adsorption are shown in Figure 4.15 and 4.16, respectively. The equilibrium adsorption capacity (q_e) is evaluated from the slope ($1/q_e$) of linear plots obtained and found to be 188.68 mg/g and 19.96 mg/g for salicylic acid and humic acids, respectively which are in accordance with q_0 values calculated from the Langmuir equation. The calculated q_e values of salicylic acid and humic acids fairly agree with the experimental values ($q_{e,exp}$ of salicylic acid = 175.38 mg/g, $q_{e,exp}$ of humic acids = 16.35 mg/g). The rate constant of pseudo-second order equation (k_2) of 0.011 and 0.037 g/(mg·min) for salicylic acid and humic acids, respectively.

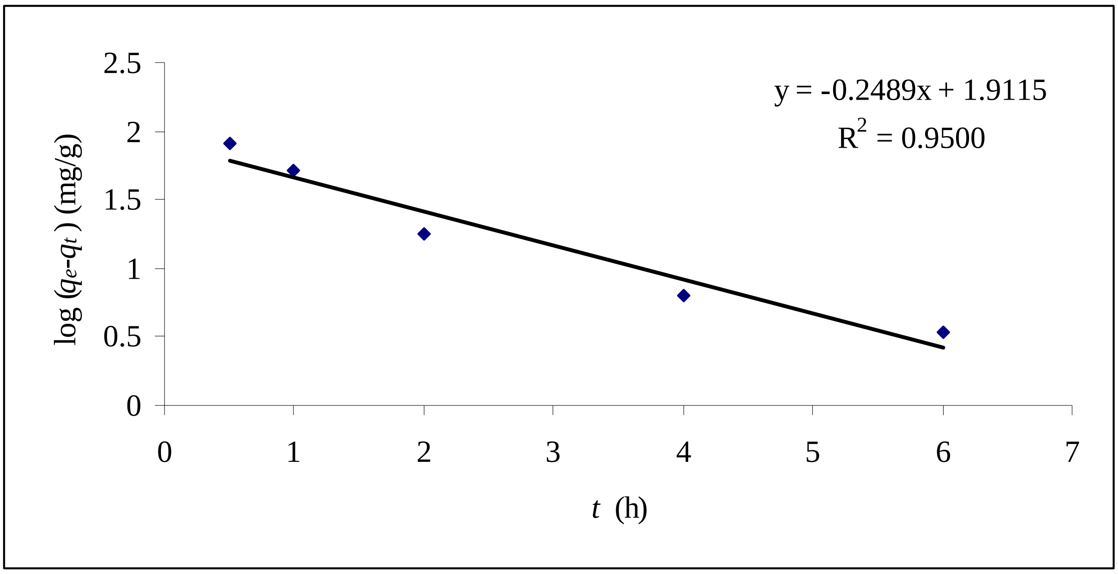

Figure 4.13 Pseudo-first order kinetic curve of adsorption of salicylic acid onto granular activated carbon; salicylic acid concentration = 400 mg/L, pH = 1, volume = 10 mL, granular activated carbon = 10 mg.

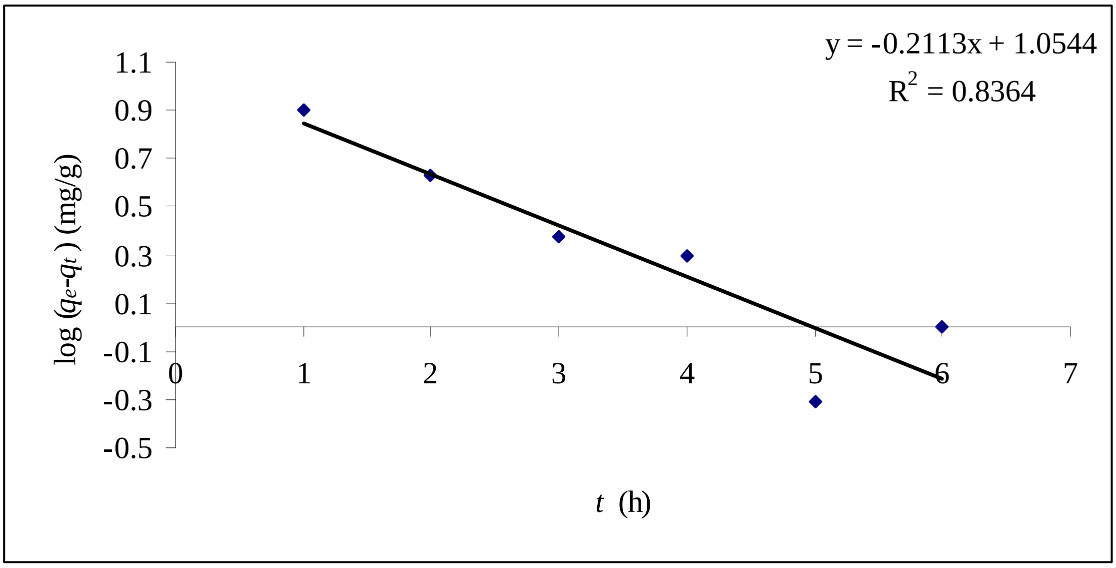

Figure 4.14 Pseudo-first order kinetic curve of adsorption of humic acids onto granular activated carbon; humic acids concentration = 100 mg/L, pH = 4, volume = 10 mL, granular activated carbon = 10 mg.

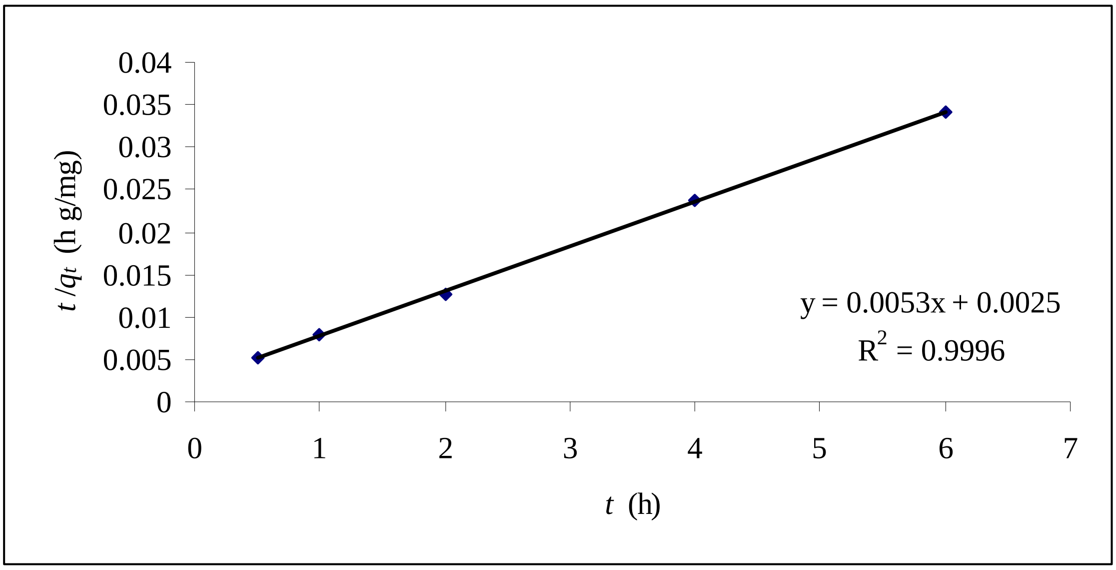

Figure 4.15 Pseudo-second order kinetic curve of adsorption of salicylic acid onto granular activated carbon; salicylic acid concentration = 400 mg/L, pH = 1, volume = 10 mL, granular activated carbon = 10 mg.

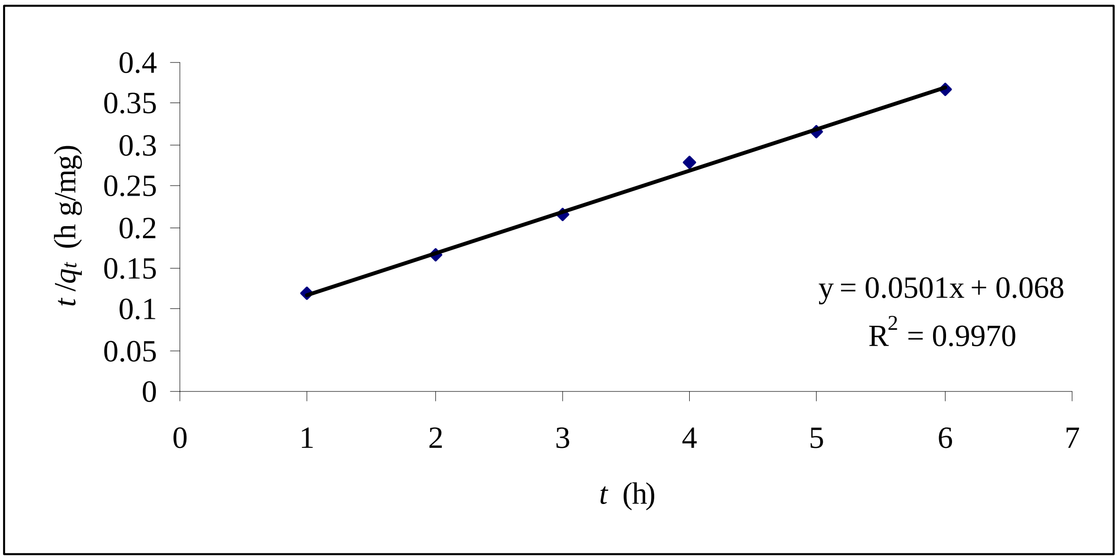

Figure 4.16 Pseudo-second order kinetic curve of adsorption of humic acids onto granular activated carbon; humic acids concentration = 100 mg/L, pH = 4, volume = 10 mL, granular activated carbon = 10 mg.

4.2.6 Simultaneous adsorption

As shown in Table 4.5, the adsorption capacity of simultaneous adsorption of salicylic acid and humic acids on granular activated carbon decreased from individual adsorption of salicylic acid and humic acids on granular activated carbon. The reduction in adsorption capacity is attributed to the competition of adsorption of salicylic acid and humic acids on granular activated carbon surface. The reduction percentage in adsorption capacity of simultaneous adsorption of salicylic acid was more than that of humic acids. It could be noticed that the initial pH of the mixed solution was 4, which was higher than the pK_a of salicylic acid. Salicylic acid was more dissociated at this pH which led to high solubility and poor adsorption (section 4.2.1). In addition, the adsorption of salicylic acid was predicted as monolayer which depends on available active sites on the activated carbon surface. In simultaneous system, some active sites was occupied by humic acids, resulting in less active sites available for salicylic acid adsorption. Thus, the reduction percentage (~42%) is higher than that of humic acids (~25%). However, the absorption might decrease in the presence of other organic compounds because of the competition between those compounds.

Table 4.5 Individual adsorption and simultaneous adsorption of salicylic acid and humic acids on granular activated carbon; salicylic acid concentration = 400 mg/L, humic acids concentration = 100 mg/L, pH = 4, volume = 10 mL, granular activated carbon = 10 mg, adsorption time = 4 hours.

Adsorbate	Individual	Simultaneous	Reduction percentage
	q (mg/g)	*q* (mg/g)	(%)
Salicylic acid	175.38±6.7	101.08±5.2	42.4
Humic acids	16.35±1.0	12.25±0.5	25.1

$$\text{Reduction percentage, \%} = \frac{q_{individual} - q_{simultaneous}}{q_{individual}} \times 100 \tag{4.4}$$

4.3 Desorption study

The amount of adsorbate desorbed (mg/g) at time *t* was calculated by

$$\text{Amount of desorption} = \frac{(C_t - C_0)V}{w} \tag{4.5}$$

where C_0 = 0 in the desorption process, C_t is the liquid-phase concentration (mg/L) at time $t = t$, V is the volume of solution (L), and w is the weigh of the adsorbent (g).

The percentage of elution was calculated from the following expression:

Elution (%) = (amount of desorption/amount of adsorption)×100 (4.6)

4.3.1 Effect of eluent type

Various eluting solution were used to identify the best eluent for desorption of salicylic acid and humic acids from granular activated carbon. NaOH with ethanol were used as eluent for desorption of salicylic acid and humic acid from granular activated since pH of eluent is higher than pH_{PZC} of granular activated carbon and pK_a of salicylic acid and humic acids. In these eluents, salicylic acid, humic acids and granular activated carbon surface are negatively charged. Considering these charges and electrostatic interactions, it is understandable to observe the high desorption in the eluent, because the surface and salicylic acid are the same negative charge. Moreover, ethanol in eluent can assist hydrophobic part of the salicylic acid and humic acids to dissolve in the eluent. The results were summarized in Table 4.6 and 4.7. NaOH with ethanol provided higher elution efficiency compared to ethanol and NaOH solution. The highest elution was obtained for 10% NaOH in 60% (v/v) ethanol/water. Finally, 5% NaOH in 10% (v/v) ethanol/water was specified as the eluent for desorption of salicylic acid and humic acids from granular activated carbon due to its high elution efficiency and less chemical substance required. The elution efficiency of 5% NaOH in 10% (v/v) ethanol/water and 10% NaOH in 60% (v/v) ethanol/water was not significantly different in pair t-test at the confidence level of 95%.

Table 4.6 Effect of eluent type for desorption of salicylic acid from granular activated carbon; salicylic acid concentration = 400 mg/L, eluent volume = 10 mL, granular activated carbon = 10 mg, contact time = 60 min

Eluting solution	Elution, %
Ethanol (absolute)	14.2±2.1
5% NaOH	69.4±2.2
5% NaOH in 10% (v/v) ethanol/water	81.6±2.3
10% NaOH in 10% (v/v) ethanol/water	84.7±3.6
10% NaOH in 60% (v/v) ethanol/water	88.6±3.4

The heterogeneous solution was formed using the ethanol amount more than 60% (v/v). Thus higher percentage of ethanol was not investigated.

Table 4.7 Effect of eluent type for desorption of humic acids from granular activated carbon; humic acids concentration = 100 mg/L, eluent volume = 10 mL, granular activated carbon = 10 mg, contact time = 60 min

Eluting solution	Elution, %
Ethanol (absolute)	4.3±0.9
5% NaOH	42.9±1.0
5% NaOH in 10% (v/v) ethanol/water	63.7±2.3
10% NaOH in 10% (v/v) ethanol/water	66.3±4.4
10% NaOH in 60% (v/v) ethanol/water	70.8±3.1

4.3.2 Effect of elution time

The effect of elution time on desorption of salicylic acid from granular activated carbon is shown in Figure 4.17. Desorption of salicylic acid increased in 15-30 min, and then desorption rate was constant in about 60 min. As shown in Figure 4.18, the desorption of humic acids increased in 15-60 min, and remained constant until 180 min. The desorption percentages at 60 min and 80 min were not significantly difference. 60 min was selected for subsequent work.

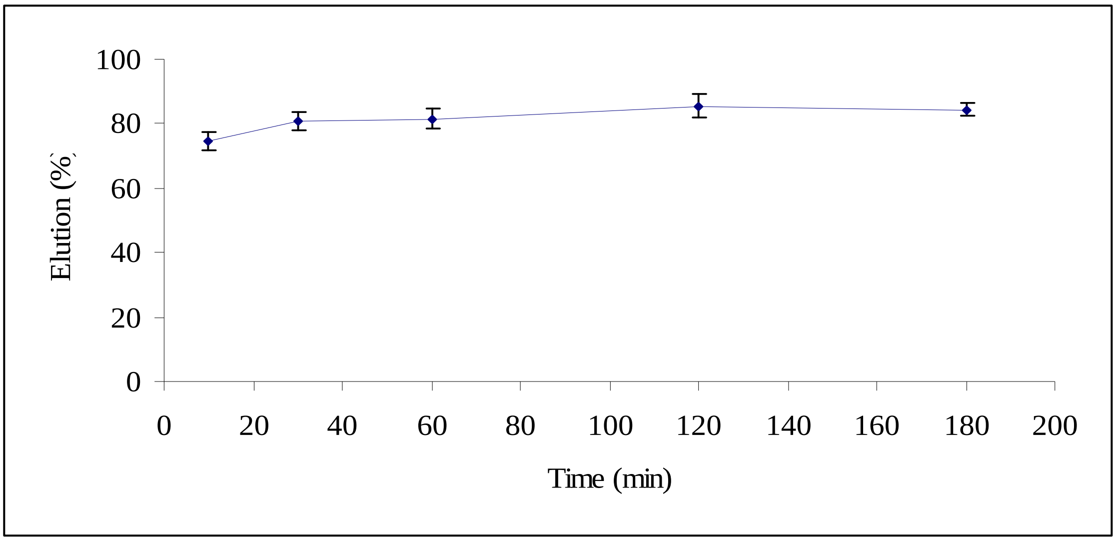

Figure 4.17 Effect of desorption time of salicylic acid; salicylic acid concentration = 400 mg/L, pH = 1, volume = 10 mL, 5% NaOH in 10% (v/v) ethanol/water = 10 mL, granular activated carbon = 10 mg.

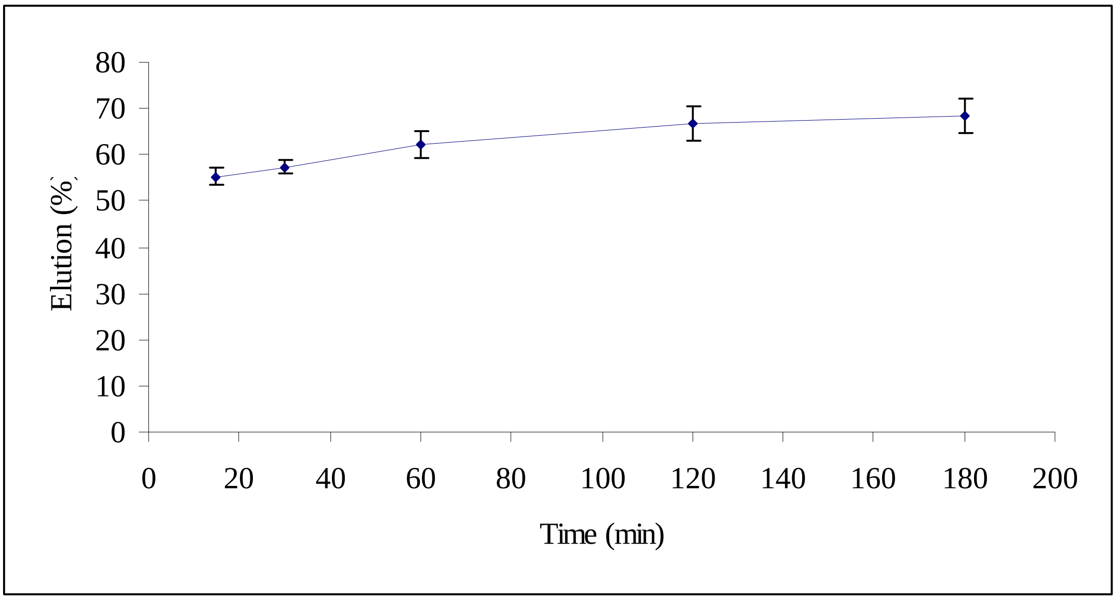

Figure 4.18 Effect of desorption time of humic acids; humic acids concentration = 100 mg/L, pH = 4, volume = 10 mL, 5% NaOH in 10% (v/v) ethanol/water = 10 mL, granular activated carbon = 10 mg.

4.3.3 Desorption kinetics

The pseudo-first order and pseudo-second order kinetic models are shown in Eqs. (4.6) and (4.7), respectively

$$\log(q - q_e) = \log(q_0 - q_e) - k_{d,1}t \qquad (2.10)$$

$$\frac{1}{(q - q_e)} - \frac{1}{(q_0 - q_e)} = k_{d,2}t \qquad (2.12)$$

where q_e, q_0 and q are the amount of adsorbate on the adsorbent at the equilibrium, at the initial and at time t, respectively (mg/g), $k_{d,1}$ is the rate constant of first-order desorption (min^{-1}), and $k_{d,2}$ is the second-order rate constant with a unit of g/(mg·min).

Table 4.8 Pseudo-first order and pseudo-second order kinetic parameters of salicylic acid and himic acids desorption from granular activated carbon

Adsorbate	$q_{e,exp}$ (mg/g)	First-order kinetic model			Second-order kinetic model		
		$q_{e,cal}$ (mg/g)	$k_{d,1}$ (min^{-1})	R^2	$q_{e,cal}$ (mg/g)	$k_{d,2}$ (g/mg·min)	R^2
Salicylic acid	19.44	106.50	0.014	0.9802	126.51	0.025	0.8781
Humic acids	4.86	11.14	0.008	0.9786	24.47	0.020	0.9503

The experimental desorption data of salicylic acid and humic acids from the granular activated carbon are fitted with the pseudo-first order kinetic model, as shown in Figure 4.19 and 4.20, but are not fitted with the pseudo-second order kinetic model as shown in Figure 4.21 and 4.22, respectively. The amount of adsorbate on the adsorbent at the equilibrium (q_e) found to be 106.50 mg/g and 11.14 mg/g for salicylic acid and humic acids, respectively. The rate constant of pseudo-first order equation ($k_{d,1}$) of 0.014 and 0.008 min^{-1} for salicylic acid and humic acids, respectively.

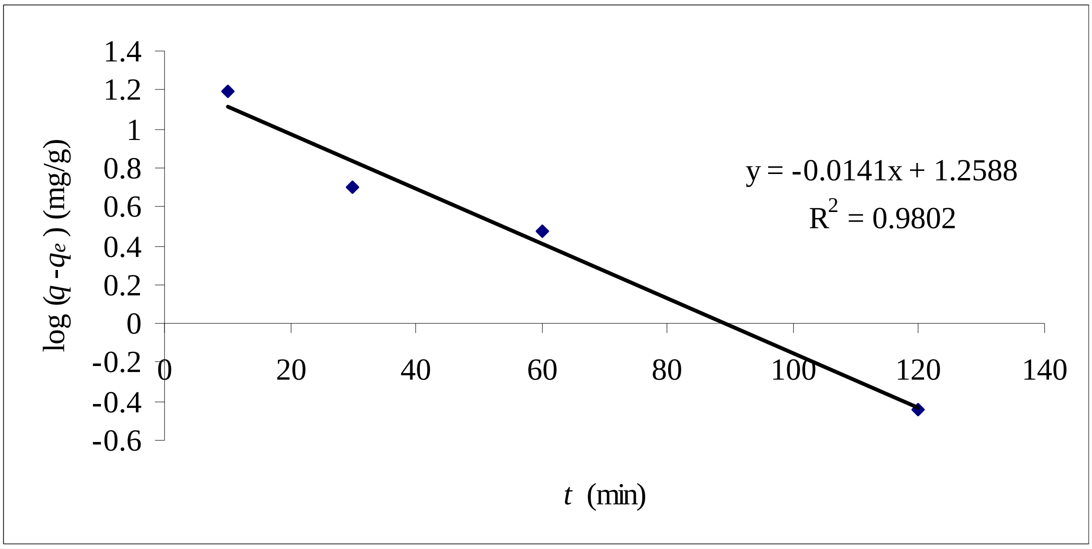

Figure 4.19 Pseudo-first order kinetic curve of desorption of salicylic acid from granular activated carbon; salicylic acid concentration = 400 mg/L, pH = 1, volume = 10 mL, granular activated carbon = 10 mg, 5% NaOH in 10% (v/v) ethanol/water = 10 mL, contact time 60 min.

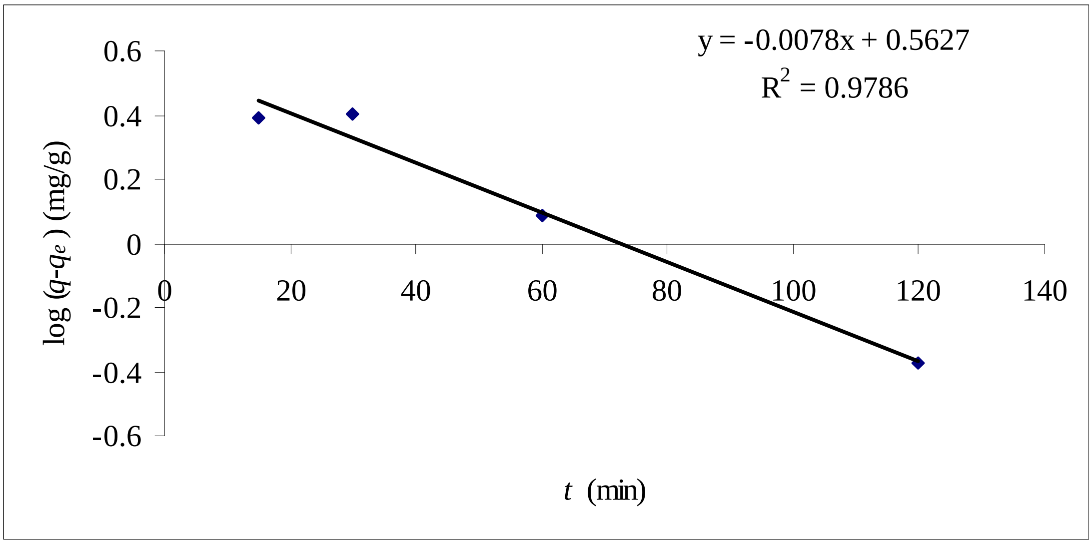

Figure 4.20 Pseudo-first order kinetic curve of desorption of humic acids from granular activated carbon; humic acids concentration = 100 mg/L, pH = 4, volume = 10 mL, granular activated carbon = 10 mg, 5% NaOH in 10% (v/v) ethanol/water = 10 mL, contact time 60 min.

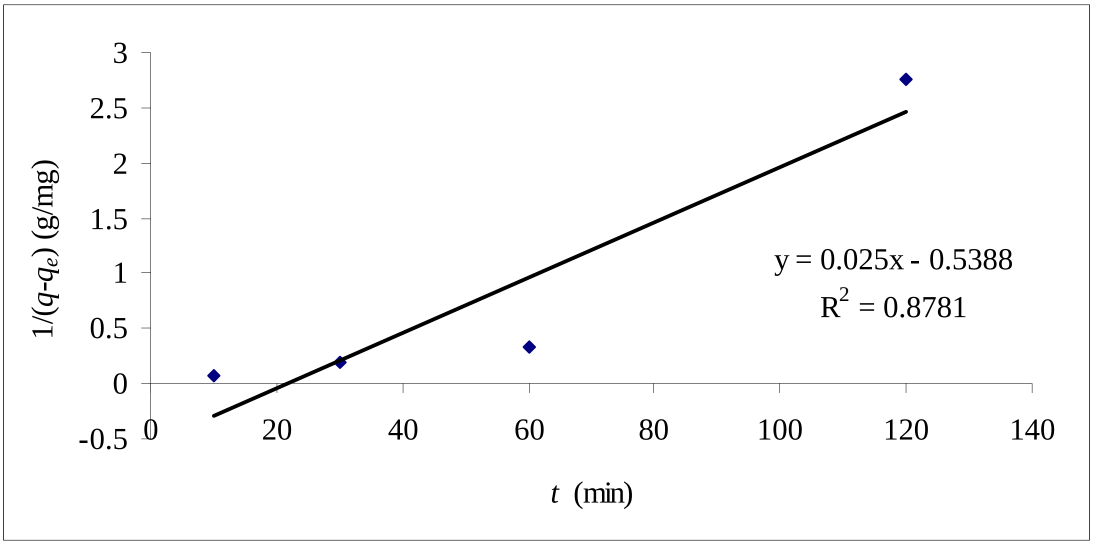

Figure 4.21 Pseudo-second order kinetic curve of desorption of salicylic acid from granular activated carbon; salicylic acid concentration = 400 mg/L, pH = 1, volume = 10 mL, granular activated carbon = 10 mg, 5% NaOH in 10% (v/v) ethanol/water = 10 mL, contact time 60 min.

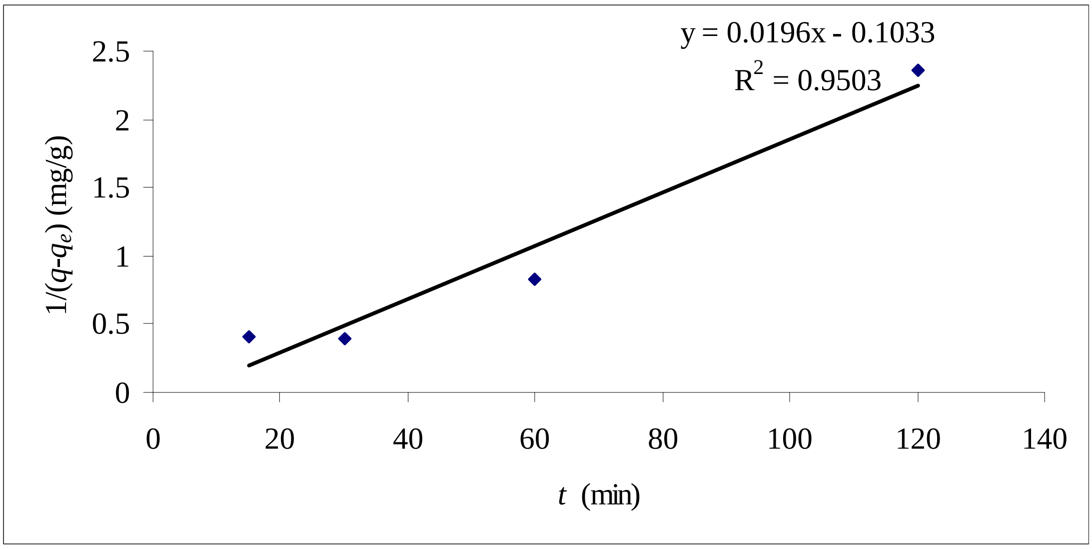

Figure 4.22 Pseudo-second order kinetic curve of desorption of humic acids from granular activated carbon; humic acids concentration = 100 mg/L, pH = 4, volume = 10 mL, granular activated carbon = 10 mg, 5% NaOH in 10% (v/v) ethanol/water = 10 mL, contact time 60 min.

4.3.4 Simultaneous desorption

As shown in Table 4.9, the percent elution of simultaneous desorption of salicylic acid and humic acids from granular activated carbon are not difference from individual desorption of salicylic acid and humic acids from granular activated carbon. This similar percent elution may be attributed to the elution capacity of the eluent used. There was no competition between salicylic acid and humic acids in desorption process. The desorption behaviour or dissolution of these two substances does not depend on the competitive or co-existing adsorbed species, but depend on their solubility in the eluent which is a constant value.

Table 4.9 Individual desorption and simultaneous desorption of salicylic acid and humic acids from granular activated carbon; salicylic acid concentration = 400 mg/L, humic acids concentration = 100 mg/L, pH = 4, volume = 10 mL, granular activated carbon = 10 mg, 5% NaOH in 10% (v/v) ethanol/water = 10 mL, contact time 60 min.

Adsorbate	Individual	Simultaneous
	Elution (%)	Elution (%)
Salicylic acid	81.6±3.0	80.7±1.8
Humic acids	62.3±3.0	61.4±3.5

4.4 Column method

The contact time in column method was calculate from Eq. 4.7

Contact time (mim) = volume of reactor (mL)/flow rate (mL/min) (4.7)

The contact time in column method for adsorption of salicylic acid and humic acids was 0.84 min, which was much lower than that of batch method (section 4.2.4).

As shown in Table 4.10, the adsorption capacity of salicylic acid and humic acids on granular activated carbon in column method decreased from batch method. The reduction in adsorption capacity because of the contact time of adsorption of salicylic acid and humic acids on granular activated carbon in column method are less than that of batch method.

As shown in Table 4.11, the percent elution of desorption of salicylic acid and humic acids from granular activated carbon decreased from batch method. The reduction in adsorption capacity was due to the fact that the contact time of desorption of salicylic acid and humic acids from granular activated carbon in column method are less than that in batch method.

Table 4.10 Adsorption of salicylic acid and humic acids on granular activated carbon in batch and column method; salicylic acid concentration = 400 mg/L, humic acids concentration = 100 mg/L, pH of salicylic acid solution = 1, pH of humic acids solution = 4, volume = 10 mL, granular activated carbon = 10 mg, flow rate = 0.5 mL/min.

Adsorbate	Batch method	Column method
	q (mg/g)	*q* (mg/g)
Salicylic acid	175.38±6.7	48.45±2.1
Humic acids	16.35±1.0	8.19±1.0

Table 4.11 Desorption of salicylic acid and humic acids from granular activated carbon in batch and column method; salicylic acid concentration = 400 mg/L, humic acids concentration = 100 mg/L, pH of salicylic acid solution = 1, pH of Humic acids solution = 4, volume = 10 mL, granular activated carbon = 10 mg, flow rate = 0.5 mL/min, 5% NaOH in 10% (v/v) ethanol/water = 10 mL.

Adsorbate	Batch method	Column method
	Elution (%)	Elution (%)
Salicylic acid	81.6±3.0	43.15±1.4
Humic acids	62.3±3.0	29.93±2.9

4.5 Regeneration study

As shown in Figure 4.23 and 4.24, the efficiency of granular activated carbon to adsorb salicylic acid and humic acids decreases as the number of adsorption-regeneration cycle increases. The reduction in efficiency is attributed to the incomplete elution of the sorbed salicylic acid and humic acids on the granular activated carbon. Therefore, the efficiency decreased each time the adsorbents were reused. After fives cycles of use, the adsorption capacity decreased by 70% of the first cycle.

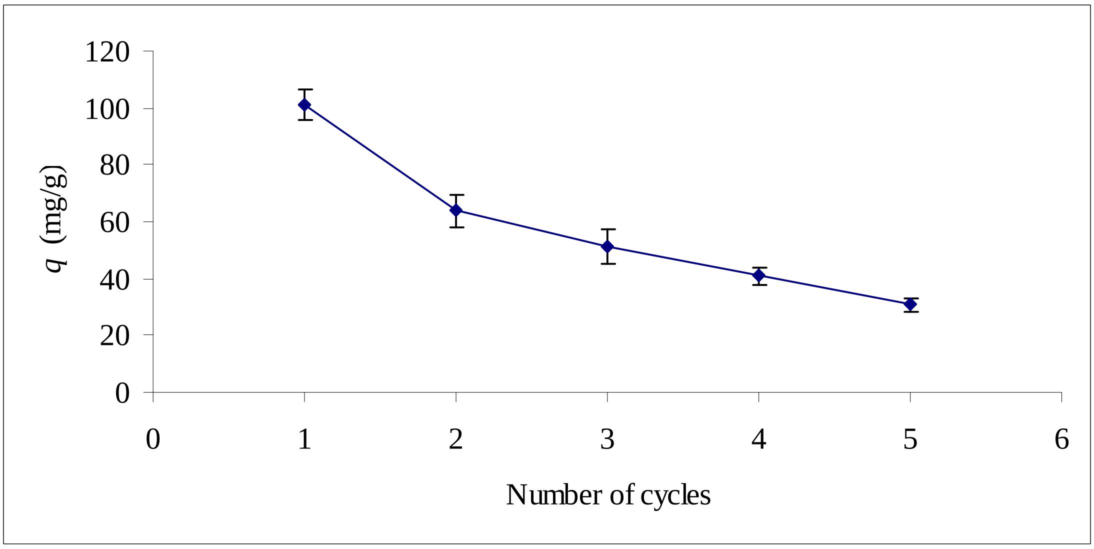

Figure 4.23 Reuse of the granular activated carbon in adsorption of salicylic acid; salicylic acid concentration = 400 mg/L, pH = 4, volume = 10 mL, granular activated carbon = 10 mg, 5% NaOH in 10% (v/v) ethanol/water = 10 mL, contact time 60 min.

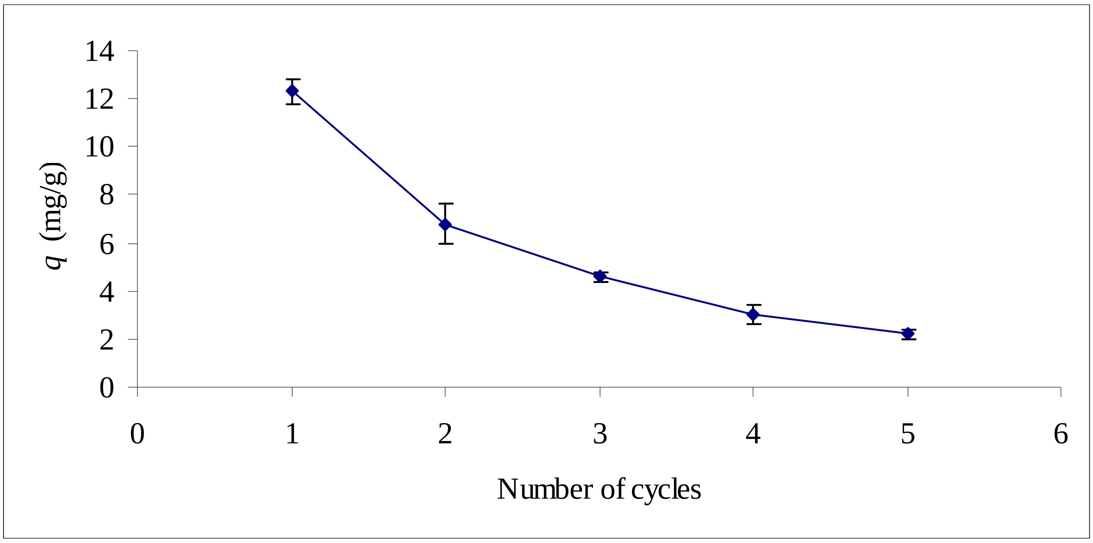

Figure 4.24 Reuse of the granular activated carbon in adsorption of humic acids; humic acids concentration = 100 mg/L, pH = 4, volume = 10 mL, granular activated carbon = 10 mg, 5% NaOH in 10% (v/v) ethanol/water = 10 mL, contact time 60 min.

CHAPTER V

CONCLUSION

The following conclusions from this study have been drawn:

1. The optimal conditions for adsorption of salicylic acid were found as follows, initial pH 1.0, initial concentration 400 ppm and contact time 4 hours. Adsorption behavior of salicylic acid followed Langmuir adsorption isotherm. The maximum adsorption capacity of the granular activated carbon for adsorption of salicylic acid is 175.4 mg/g. The rate of adsorption could be predicted with the pseudo second order model.

2. The optimal conditions for adsorption of humic acids were found as follows, initial pH 4.0, initial concentration 100 ppm and contact time 4 hours. Adsorption behavior of humic acids followed Freundlich adsorption isotherm. The maximum adsorption capacity of the granular activated carbon for adsorption of humic acid is 16.3 mg/g. The rate of adsorption could be predicted with the pseudo second order model.

3. The optimal conditions for simultaneous adsorption of salicylic acid and humic acids were found as follows, initial pH 4.0, initial concentration of salicylic acid and humic acids are 400 and 100 ppm, respectively. The maximum adsorption capacity of the granular activated carbon for adsorption of salicylic acid and humic acids are 101.1 and 12.2 mg/g, respectively and the equilibrium time was 4 hours.

4. The optimal conditions for desorption of salicylic acid and humic acids from granular activated carbon were found to be 5% NaOH in 10% ethanol/water as eluent and 1 hour desorption time. The elution percentages of salicylic acid and humic acids from granular activated carbon were 81.6 and 62.3%, respectively.

5. The reuse of granular activated carbon for salicylic acid and humic acids after regeneration was possible. However, the adsorption efficiency decreased gradually upon reuse cycles.

Suggestion for future work

1. To study other types of granular activated carbon and other commercial adsorbents.
2. To study effect of major interfering ions present in water or wastewater to be treated.
3. To study recirculation in column method for adsorption and desorption of salicylic acid and humic acids on granular activated carbon.

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