การดูดซับอาร์เซไนต์และอาร์เซเนตโดยยางรถยนต์เหลือทิ้งดัดแปรด้วย พอลิ (3-อะคริลามิโดโพรพิล)ไตรเมทิลแอมโมเนียมคลอไรด์

นางสาวทิตยติ สิริทวีสิทธิ์

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ADSORPTION OF ARSENITE AND ARSENATE BY POLY(3-ACRYLAMIDOPROPYL) TRIMETHYLAMMONIUM-CHLORIDE-MODIFIED WASTE TYRE RUBBER

Miss Thitayati Sirithaweesit

A Thesis Submitted in Partial Fulfillment of the Requirements
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Thesis Title	ADSORPTION OF ARSENITE AND ARSENATE BY POLY(3-ACRYLAMIDOPROPYL)TRIMETHYLAMMONIUM-CHLORIDE-MODIFIED WASTE TYRE RUBBER
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ทิตยติ สิริทวีสิทธิ์ : การดูดซับอาร์เซไนต์และอาร์เซเนตโดยยางรถยนต์เหลือทิ้งดัดแปรด้วยพอลิ (3-อะคริลามิโดโพรพิล)ไตรเมทิลแอมโมเนียมคลอไรด์. (ADSORPTION OF ARSENITE AND ARSENATE BY POLY(3-ACRYLAMIDOPROPYL)TRIMETHYLAMMONIUM-CHLORIDE-MODIFIED WASTE TYRE RUBBER) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ. ดร.อภิชาติ อิ่มยิ้ม, 78 หน้า.

ได้เตรียมผงยางรถยนต์เหลือทิ้งดัดแปรด้วยพอลิ(3-อะคริลามิโดโพรพิล)ไตรเมทิลแอมโมเนียมคลอไรด์ซึ่งเป็นพอลิเมอร์ที่มีประจุบวก โดยสังเคราะห์ผ่านปฏิกิริยาฟรีเรดิคอลพอลิเมอไรเซชันในสารละลาย นำวัสดุที่เตรียมได้ WTR/p(APTMACl) มาใช้เป็นตัวดูดซับอาร์เซไนต์และอาร์เซเนตออกจากสารละลายที่อุณหภูมิห้อง วัสดุที่เตรียมได้มีประสิทธิภาพในการดูดซับอาร์เซไนต์และอาร์เซเนตผ่านทางการดูดซับทางกายภาพและการแลกเปลี่ยนไอออน ศึกษาปัจจัยที่มีผลต่อการเตรียมและการนำไปใช้ดูดซับอาร์เซไนต์ และอาร์เซเนตของ WTR/p(APTMACl) ทั้งในระบบแบทช์และคอมลัมน์ พีเอชที่เหมาะสมในการดูดซับอาร์เซไนต์และอาร์เซเนตคือ 6 และ 8 ตามลำดับ การดูดซับเพิ่มขึ้นเมื่อเพิ่มความเข้มข้นของมอนอเมอร์และระยะเวลาในการดูดซับ เมื่อเปรียบเทียบอุณหภูมิในการทำให้คอมโพสิตแห้งระหว่าง 50 และ 100 องศาเซลเซียส พบว่าการดูดซับอาร์เซเนตสูงเมื่อใช้อุณหภูมิต่ำ พฤติกรรมการดูดซับอาร์เซไนต์และอาร์เซเนตเกิดขึ้นเป็นไปตามฟรุนด์ลิชไอโซเทอร์มด้วยค่าสัมประสิทธิ์ความเป็นเส้นตรง (R^2) มากกว่า 0.91 และ 0.98 ตามลำดับ ซึ่งหมายความว่าการดูดซับเกิดขึ้นบริเวณพื้นผิวแบบเฮเทอโรจีเนียส อัตราเร็วในการดูดซับอาร์เซไนต์และอาร์เซเนตสามารถทำนายด้วยสมการอัตราการเกิดปฏิกิริยาอันดับสองเทียม นอกจากนี้ยังได้นำตัวดูดซับมาใช้ในระบบคอลัมน์ในการดูดซับอาร์เซไนต์และอาร์เซเนตด้วยอัตราการไหล 0.85 มิลลิลิตรต่อนาที การดูดซับของอาร์เซเนตเกิดได้ดีกว่าอาร์เซไนต์ โดยให้ค่าการดูดซับของอาร์เซไนต์และอาร์เซเนตที่ 0.014 และ 0.077 มิลลิกรัมต่อกรัมตามลำดับ และการประสิทธิภาพการดูดซับในระบบคอลัมน์ต่ำกว่าการดูดซับในระบบแบทช์ การชะอาร์เซไนต์และอาร์เซเนตออกจากตัวดูดซับสามารถเกิดขึ้นได้โดยใช้สารละลายกรดไฮโดรคลอริกความเข้มข้น 0.10 โมลาร์เป็นตัวชะ นอกจากนี้ยังมีความเป็นไปได้ในการนำตัวดูดซับมาทำการดูดซับอาร์เซนิกออกจากน้ำเสียจากโรงงานอุตสาหกรรม

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THITAYATI SIRITHAWEESIT: ADSORPTION OF ARSENITE AND ARSENATE BY POLY(3-ACRYLAMIDOPROPYL)TRIMETHYLAMMONIUM-CHLORIDE-MODIFIED WASTE TYRE RUBBER. ADVISOR: ASST. PROF. APICHAT IMYIM, Ph.D., 78 pp.

Waste tyre rubber (WTR) powder was modified with cationic polymer, poly(3-acrylamidopropyl)trimethylammonium chloride (p(APTMACl)) which was synthesized by free radical polymerization in aqueous solution. The resulting WTR/p(APTMACl) was utilized as adsorbent for the adsorption of arsenite and arsenate from aqueous medium at room temperature. It was effective in the adsorption of arsenite and arsenate via physisorption and ionic exchange. Various parameters were optimized the preparation and utilization of this WTR/p(APTAMCl) for arsenite and arsenate adsorption in both batch and column methods. The optimal pH for the arsenite and arsenate adsorption was 6 and 8, respectively. The adsorption increased gradually with increasing the monomer concentration and contact time. Comparing drying temperatures between 50 and 100 °C, the adsorption amount of arsenate was higher at the lower drying temperature. The arsenite and arsenate adsorption behavior obeyed the Freundlich model with the R^2 of more than 0.91 and 0.98, respectively, indicating that the adsorption occurred on a heterogeneous surface. The rate of arsenite and arsenate adsorption could be predicted with the pseudo-second order model. The sorbent was subsequently packed into a column and used for the adsorption of arsenite and arsenate with an optimized flow rate at 0.85 mL/min with a weight of 0.65 g. In the column method, arsenate could be adsorbed onto the sorbent better than arsenite. Arsenite and arsenate extraction was 0.014 and 0.077 mg/g, respectively. Both of these two arsenic species showed lower adsorpabilty than that in the batch method. The remarkable desorption of arsenite and arsenate from the sorbent using 0.10 M HCl as eluent was achieved as 99 and 92%, respectively. Moreover, the sorbent showed a promising adsorption of arsenic from real wastewater.

Field of Study:	Petrochemistry and Polymer Science	Student's Signature	....
		Advisor's Signature	....
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LIST OF ABBREVIATIONS

WTR = Waste tyre rubber

p(APTMACl) = Poly(3-acrylamidopropyl)trimethylammonium chloride

WTR/p(APTMACl) = Poly(3-acrylamidopropyl) trimethylammonium-chloride-modified waste tyre rubber

NR = Natural rubber

SBR = Stylene-butadiene rubber

BD = Butadiene

FT-IR = Fourier transform infrared spectrometer

g = Gram

L = Liter

mL = Milliliter

CHAPTER I
INTRODUCTION

1.1 Statement of the problem

Arsenic (As) is a metallic element that naturally occurs within the earth. It has been used in various fields such as agriculture, livestock, electronics industry, and metallurgy because of its toxicity and highly effective conducting material. Arsenic is toxic to plants and animals. Inorganic arsenic compounds are stimulation carcinogens in human. The toxicity of arsenic to human health ranges from skin lesion to cancer of the brain, liver, kidney, and stomach [1]. Moreover, arsenic and its compounds are ability mobile in the environment by dissolution in rain, river or groundwater. Arsenic has been detected in groundwater in several countries, with concentration levels exceeding the World Health Organization (WHO) drinking water guideline that regulates the value of 10 μg/L [2]. Therefore, remediation of As-contaminated water is critical and necessary.

A wide range of methods has been used to remediate As-contaminated water such as phytoremediation, chemical oxidation, photochemical oxidation, and photocatalytic oxidation. However, they are also quite complex and expensive. Adsorption technique is an interesting method for the remediation of arsenic because of its easily available, cheap, and ability regenerated. Many researchers have focused on finding low-cost adsorbents and several adsorbents such as TiO_2 [3], chars [4], red mud [5], iron oxide-loaded slag [6], and waste tyre rubber [7].

Nowadays, the number of waste tyre rubber (WTR) from vehicle industry is increasing every year. As a result, waste tyre rubber has become a great concern in the management and disposal. The carbon black used to reinforce the rubber, is similar to activated carbon and offers as a good adsorbent to remove organic substances from wastewater [8]. Previous works have been reported numerous uses on the adsorption of heavy metals from water and wastewater by waste tyre rubber.

Therefore, waste tyre rubber is an interesting for the preparation of adsorbent materials that may be useful for the removal of arsenic from solutions.

Some of the problems associated with the use of waste tyre rubber are limited sorption capacity and slow adsorption kinetics. Therefore, in this study, we purpose to enhance arsenic adsorption capacity by modification of waste tyre rubber with reclamation by microwave method and by coating with a cationic polymer; poly(3-acrylamidopropyl)trimethylammonium chloride.

1.2 Scope of the research

The scope of this research was firstly characterization of the waste tyre rubber. Then the waste tyre rubber was modified by microwave method and poly(3-acrylamidopropyl)trimethylammonium chloride with the modifying condition optimized for arsenic extraction through batch method. After that, the adsorption isotherm and contact time of the arsenic extraction were studied. Then, the column extraction was evaluated by taking into account of the effect of flow rate, desorption of adsorbent, and breakthrough curve. Finally, the column of modified adsorbent was utilized to remove arsenic from real industrial wastewater.

1.3 Benefits of this research

Poly(3-acrylamidopropyl) trimethylammonium-chloride-modified waste tyre rubber was prepared and used as sorbent for arsenite and arsenate adsorption from wastewater.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Arsenic

2.1.1 Properties of arsenic

Arsenic is a metallic element. It can be both a metal and non-metal, and its compounds occur in liquid, solid, and gaseous forms. Natural arsenic features silver-grey brittle crystalline solid and serves as a highly effective conducting material. The physical properties of arsenic are shown in Table 2.1.

Table 2.1 Physical properties of arsenic

Physical properties	
Atomic number	33
Molar atomic weight	74.9216 g.mol^{-1}
Melting point	81.7 °C
Boiling point	613 °C
Density	5.727 g.cm^{-3}
Electronegativity	2.18

2.1.2 Arsenic species

Arsenic, like other metalloids, is sensitive to both redox state and pH of the chemical environment and could be form both of inorganic and organic forms in water. Arsenic exists in four oxidation states, +V (arsenate), +III (arsenite), 0 (arsenic), and –III (arsine). Arsenic naturally occurs in many different mineral forms, of which approximately 60% are arsenates, 20% sulfides and sulfosalts and the remaining 20%

includes arsenites, arsenides, oxides, silicate and elemental arsenic [9]. The molecular formulas of organic compounds are shown in Table 2.2 [10].

The most common forms of arsenic in the environment are the inorganic oxyanions, of which arsenite (AsO_3^{3-}) and arsenate (AsO_4^{3-}) referred to arsenic (III) and arsenic (V), respectively. Arsenite species or trivalent (+3) are $As(OH)_3$, $As(OH)_4^-$, AsO_2OH^{2-}, and AsO_3^{3-} while arsenate species or pentavalent (+5) include AsO_4^{3-}, $HAsO_4^{2-}$, and $H_2AsO_4^-$.

Table 2.2 The molecular formula of organic compounds

Name	Structure	Name	Structure
Methylarsine	CH_3AsH_2	Dimethylarsenous acid	$(CH_3)_2AsOH$, DMA^{III}
Dimethylarsine	$(CH_3)_2AsH$	Trimethylarsinic oxide	$(CH_3)_3AsO$, TMAO
Trimethylarsine	$(CH_3)_3As$	Tetramethylarsonium ion	$(CH_3)_4As^+$, TMA^+
Monomethylarsonic acid	$CH_3AsO(OH)_2$, MMA^V	Arsenobetine	$(CH_3)_3As^+CH_2COO^-$, AB
Monomethylarsenous acid	$CH_3As(OH)_2$, MMA^{III}	Arsenocholine	$(CH_3)As^+CH_2CH_2OH$, AC
Dimethylarsinic acid	$(CH_3)_2AsO(OH)$, DMA^V		

Arsenite is more toxic and relatively mobile in contaminated soils, whereas arsenate is relatively less toxic. However, in water, the relative proportion of two species varies depending on a number of factors, including arsenic sources, redox potential and pH.

Both arsenite and arsenate are sensitive to mobilization in water. Under moderately reducing anaerobic environments such as groundwater arsenites are the predominant arsenic compounds. Arsenic(III) is a hard acid and preferentially complexes with nitrogen and oxides. Under oxidizing conditions, in oxygen rich aerobic environments, arsenates are the stable species and behave like a soft acid which forming complexes with sulfides [9, 11]. Arsenic species predominate in various pH. The distributions of arsenic species as a function of pH are summarized in Figure 2.1.

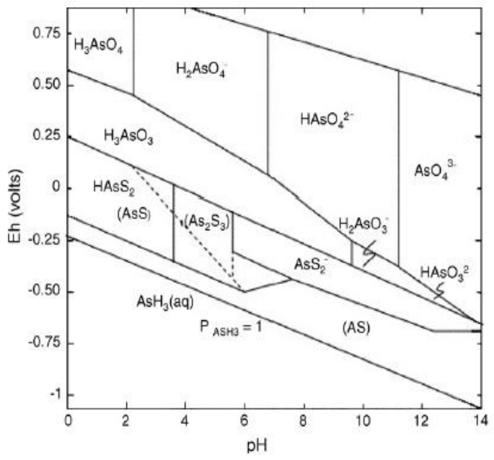


Figure 2.1 The redox potential-pH or Eh-pH diagram for arsenic at 25 °C and 101.3 kPa [11].

2.1.3 Remediation of arsenic

Arsenic is a well-known as one of the world’s most hazardous chemicals. There have many sites which have been contaminated by arsenic from natural and anthropogenic sources. Remediation of arsenic from water is essential. Therefore, the sustainable and eco-friendly methods for remediation of arsenic were studied.

2.1.3.1 Adsorption

Adsorption method has importance in industry and environmental protection. It is a simple method for the removal of several metal ions. Adsorption processes are used for separation and purification because of the high reliability, energy efficiency, design flexibility, technological development and ability to regenerate the exhausted adsorbent. The process of adsorption involves separation of a substance from one phase accompanied by its concentration or accumulation at the surface of another. Adsorption can be resulted from Van der Waals interactions and electrostatic forces between adsorbate molecules and the atoms of the adsorbent surface (physical adsorption, physisorption), or it can have the character of a chemical process (chemical adsorption, chemisorptions) [12]. Activated carbon was the first generally used adsorbent but it removes only a few milligrams of arsenic. This lead to have the problem of regeneration of spent adsorbent if activated carbon is used. Therefore, the other adsorbents, which have equal or greater efficiency than activated carbon for removal of arsenic such as activated alumina, ion-exchange resins, sand, silica, clays, iron compounds, and organic polymers, have been interesting [11].

2.1.3.2 Phytoremediation

Phytoremediation, plant based on environmental-friendly technology, has appropriated attention. The discovery of terrestrial and aquatic plants is able to remediate contaminated soils and waters, respectively. A number of aquatic plant species have been investigated for the remediation of toxic contaminants such as As, Zn, Cd, Cu, Pb, Cr, Hg, etc. Some aquatic plants species such as water hyacinth (*Eichhornia crassipes*), duck weeds (*Lemna gibba, Lemna minor, Spirodela polyrhiza*), water spinach (*Ipomoea aquatic*) have been investigated their arsenic uptake ability and to assess their potential in phytoremediation technology [13, 14]. Mechanisms for arsenic remediation by plants are hypothesized that hyper accumulation is associated with the interaction of arsenic with high-affinity chelating molecules present in the cytoplasm of the plant. This lead to the major benefit of phytoremediation is that the above-ground vegetative biomass is not contaminated with arsenic [10]. Phytoremediation method limits uptake and prevents mobilization of arsenic. However, this method is a long-term remediation, they are not suitable for use in standard process equipment and few plants have the ability to remove high amount of arsenic.

2.1.3.3 Chemical oxidation

Most arsenic removal technologies are efficient when arsenic is in the pentavalent state (iAs^{V}), because it is presented in the form of oxyanions, mainly $H_2AsO_4^{-}$ and $HAsO_4^{2-}$ in a pH range of 2-12, while the trivalent form (iAs^{III}) is uncharged (H_3AsO_3) at a pH below 9.2 [15]. Chemical oxidation method for pollutants in wastewater is less harmful. Mechanisms occur through the addition of an oxidizing agent. During chemical oxidation, one or more electrons transfer from the oxidant to the targeted pollutant, causing its destruction. Many studies have been investigated on the oxidation of iAs^{III} by oxidizing agent such as chlorine, chlorine dioxide (ClO_2), chloroamine (NH_2Cl), ozone, hydrogen peroxide, permanganate (MnO_4^{-}), and ferrate (FeO_4^{2-}) [10, 16]. Although chemical oxidation method is effective for treatment of wastewater, it is limited for application at heavily contaminated sites and need extensive wastewater pretreatment.

2.1.3.4 Photochemical oxidation

Photochemical oxidation is very cheap technology based on the use of solar light. The use of solar light or artificial light has been studies to facilitate oxidation of iAs^{III} to iAs^{V}. A two-step process is effective to remove arsenic: one for iAs^{III} oxidation and the second for elimination of the produced iAs^{V}. Photo-oxidation processes can only occur when light is absorbed by a species and reactive free radical is produced. Therefore, no oxidation of arsenic was observed when a solution containing only iAs^{III}. Arsenite absorb light with wavelengths greater than 220 nm and the lamp produces photons with wavelengths between 300 and 400 nm [17]. This process involves the use of an oxidant to generate radicals which attack the organic pollutants to initiate oxidation. The major oxidants used are hydrogen peroxide (H_2O_2), ozone, and photo-Fenton systems (Fe^{3+}/ H_2O_2) have been evaluated. The addition of Fe^{3+} and H_2O_2 to the process increased oxidation efficiency because it generates powerful oxidants, the $HO^{\cdot}$ radicals which are effective in destroying organic chemicals. However, this method is needed high energy solar light input and the formation of toxic products and the removal of residual ozone from water are some of the significant challenges of this process [15, 18].

2.1.3.5 Photocatalytic oxidation

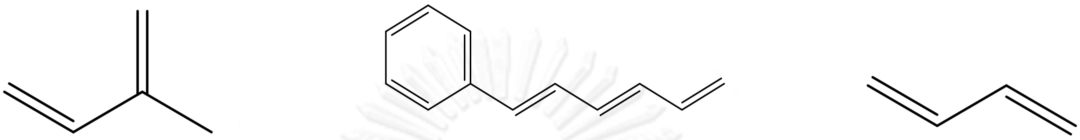
Photocatalytic oxidation, one of the low-cost technologies is based on solar or artificial light and irradiated by catalyst. The catalyst, usually a semiconductor, which may be photo-excited to form electron donor sites (reducing sites) and electron-acceptor sites (oxidizing sites). The semiconductor to be used as photo-catalyst must be photoactive, able to utilize visible and or near UV light, biologically and chemically inert, and photo-stable. The effective oxidation of iAs^{III} to iAs^{V} by photocatalytic oxidation can be achieved. There are a number of semiconductors which are readily available such as TiO_2, H_2O_2, ZnO, CdS, WO_3, and SnO_2 [19]. Among several semiconductors, the photocatalytic method using TiO_2 as a catalyst is another newly developed. It is stable to photo and chemical corrosion and inexpensive. Although photocatalytic oxidation of As species has been studied, it has a little knowledge about the effects of natural levels of sunlight over prolonged time periods on As speciation in diverse aquatic environmental system [10, 19].

2.2 Waste tyre rubber

Nowadays, rubber products are found everywhere. In automobile industry, this accounts for the largest consumption of rubber for tyres. The variety and importance of automobile accessories made of rubber continue to increase. It is possible to find a variety of rubber parts in car such as vibration damper, rubber belts, hoses, hydraulic packing rings and O-rings. Waste tyre rubber (WTR) is no longer suitable for use. Due to irreparable damage such as punctures leading to these tyres are among the largest and most problematic sources of waste because of the large volume produced and their durability.

2.2.1 Chemical/composition

Waste tyre rubber is the rubber compound that was first developed by Goodyear and Hancock and it continues to develop as new materials. It is a mixture of a number of different ingredients. It starts with the raw gum elastomeric, sourced by natural rubber or by the petroleum products such as ethylene, propylene and butadiene [20]. Then, rubber compound was mixed with some chemicals to make a rubber compound which is subsequently vulcanized. Waste tyre rubber is produced from natural or synthetic sources. It consists of a complex mixture of elastomers. The most commonly used elastomer matrix is the natural rubber (NR) or polyisoprene, the co-polymer styrene-butadiene rubber (SBR), polybutadiene (BD), or a blend of various elastomers. The structures of elastomer are shown in Figure 2.2.



isoprene styrene-butadiene butadiene

Figure 2.2 Structures of isoprene, styrene-butadiene, and butadiene.

Natural rubber (NR) is extracted from the *Hevea brasiliensis* trees in the form of latex which contains neutral lipids (2.4%), glycolipids and phospholipids (1.0%), proteins (2.2%), carbohydrate (0.4%), ash (0.2%), and other compounds (0.1%) [21]. Solid rubber consisted of mainly long-chain saturated and unsaturated fatty acids such as stearic, oleic, and linoleic acid. Saturated fatty acids influence the crystallization of rubber chain while unsaturated fatty acids which are present in natural rubber act as a plasticizer of rubber and accelerate synergistically with saturated fatty acids on the crystallization of rubber chains. Natural rubber is a very high molecular weight. It nearly 100% *cis*-1,4 polyisoprene with molecular weight ranging from 1 to 2.5 x 10^6. Natural rubber is very good dynamic mechanical properties for use in tyres. It has a very high elasticity (ability to snap back to their original shape), tear strength, and wear resistance. Moreover, the other advantages over synthetic polymers are reduced build-up of heat from flexing and greater resistance to tearing when hot. However, natural rubber is low ozone, aging, and fatigue resistance [20]. Although there are various kinds of synthetic rubber available, natural rubber is still used extensively in tyres.

Styrene-butadiene rubber (SBR) is the most common synthetic rubber used in tyres because of their suitable properties to performance needs particularly in treads of passenger car tyres. It is acquired from petroleum oil and produced by both emulsion and solution polymerization of the two major chemical building blocks styrene and butadiene. Emulsion polymerization is carried out either hot at about 50 °C or cold at about 5 °C, depending on the initiating system [22]. Styrene-butadiene rubber made in emulsion usually contains about 23% styrene randomly diffused with butadiene in the polymer chains. The processing of styrene-butadiene rubber compounds is similar to natural rubber in the procedures. Moreover, the properties of styrene-butadiene rubber are also similar to natural rubber, for chemical, solvent, and weather resistance [20, 23].

Butadiene (BR) like NR and SBR, is a common synthetic rubber used in tyres. It is a homopolymer of 1,3 butadiene. In tread compounds, butadiene rubber is usually blended at about 10% to 20% with SBR to obtain a good performance characteristic [23]. Butadiene rubber is also used in higher loading as a blend with natural rubber to enhance hysteresis (resistance to heat buildup) and abrasion resistance. It gives better low temperature flexibility and higher resilience at ambient temperature than most elastomer but poor elongation resistance [24].

To achieve the desired properties, the usual components and additives are selected according to technical as well as economic considerations. They are shown in Table 2.3.

Table 2.3 The compounds formulation of tyre (phr is defined as parts by weight of ingredient per 100 parts of rubber)[20]

Material	phr
Rubber	100
Sulfur	0-4
Zinc oxide	5
Stearic acid	2
Accelerators	0.5-3
Antioxidant	1-3
Filler	0-150
Plasticizer	0-150
Miscellaneous	0-150

Sulfur is the most used cross-linking agent. It reacts chemically with the raw rubber forming cross-links between the polymer chains that resulting in a more dimensionally stable and less heat-sensitive product. Zinc oxide reacts with stearic acid to form zince stearate and both with the accelerator to speed up the rate at which sulfur vulcanization occurs. Some accelerators such as tetramethylthiuram disulfide (TMTD) and dithiodimorpholine (DTDM) are stable to provide sulfur from their chemical structure. Sulfur donors provide monosulfidic cross-links which improved compression set and heat resistance. Moreover, fillers are used to strengthen rubber. Carbon black is reinforcing filler used to strengthen the rubber and improve abrasion resistance which commonly used in tyre [23, 25]. To give a desired product, antioxidants, age resistor, and anti-degradants are used in the production of tyre rubber.

2.2.2 Production process

Virgin rubber, both natural rubber and synthetic rubber, must be broadly processed before its use. The rubber must undergo several processes, including mixing, shaping, and vulcanizing process to achieve the desired properties.

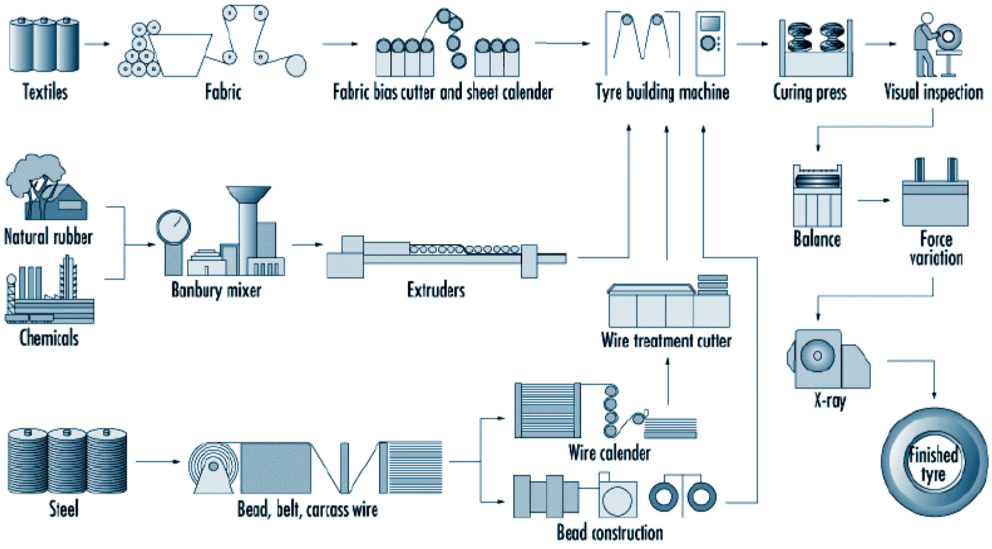


Figure 2.3 Schematic of tyre manufacture process [26].

In the first step, all components include rubber stock, carbon black, and other chemical ingredients except the vulcanizing agent (sulfur) are mixed to create a homogeneous rubber material. After the specified compound has been mixed, the molding can begin. Rubber is placed onto a drop mill to shape into flat by forcing it through two set rolls rotating in different directions at different speeds. This process includes calendaring which to obtain a sheet of rubber of uniform thickness and extrusion which shape compounds into products [26]. In the third step, curing and vulcanizing, the rubber is heated under pressure at about 150 °C for some periods [27].

Vulcanization is the thermo-chemical process, which conversions of rubber molecules into a network by formation of cross-links in order to provide the elasticity and other properties those are desired in manufactured products. The vulcanization process is irreversible at standard atmospheric conditions of temperature and pressure. The main polymers subjected to vulcanization are natural rubber (polyisoprene) and styrene-butadiene rubber, which are used for most tyres. The cured sites or reactive sites are allylic hydrogen atoms; C-H bonds which adjacent to carbon-carbon double bonds. Some of these C-H bonds are replaced by sulfur atoms in chains that like with another cured site of the polymer chains [28]. The number of sulfur atom in the crosslink influences the physical properties of the rubber product. Therefore, vulcanizing agents are necessary for this cross-linking.

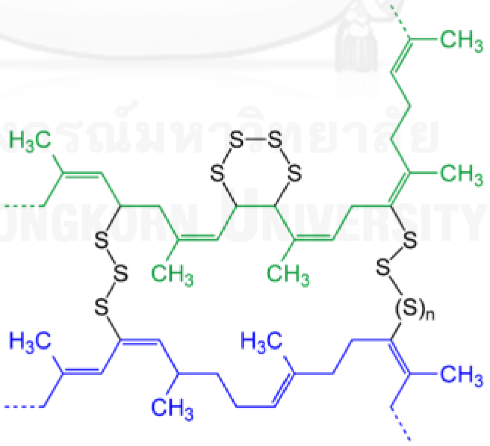


Figure 2.4 Schematic of natural rubber after vulcanization with elemental sulfur [29].

Two types of commonly vulcanizing agents or cross-linking agent are sulfur and peroxide. Sulfur is the most important cross-linking agent, which inexpensive and plentiful. Sulfur links one chain to another through double bond of rubber. The consisting of many sulfur atom would be more flexible than a cross-link consisting of a single sulfur atom and that sulfur to sulfur bond are weaker (less thermally stable) than a sulfur to carbon link. Other cross-linking agents are known as peroxides. Peroxides react with the rubber chain by removing hydrogen atoms from the carbon backbone of the polymers, resulting of radicals. The radicals attach to a similar site on another chain, creating a carbon to carbon cross-link which is stronger than sulfur to carbon link. They give a better tensile strength and expense of fatigue life [27, 29].

2.2.3 Reclamation of rubber

Since polymeric materials do not decompose easily, disposal large amount of waste tyre rubber is a serious environmental problem. Reclamation of waste tyre rubber is the most desirable advent to solve the disposal problem. Reclamation is the conversion of a three dimensionally interlinked, infusible, and insoluble to a two dimensional that is soft, plastic and tacky. However, the molecular weight of rubber is reduced, so reclaim compounds have physical properties poorer than new rubber. Reclamation can occur by breaking the existing cross-link in the vulcanized rubber or by promoting scission of the main chain of the polymer or combination of both processes. The process of reclaiming waste tyre rubber can separate into two steps. The first step or pre-processing is size reduction. The waste tyre rubber is reduced in size without chemical bond breaking. The second step is the devulcanization process.

Devulcanization is the process of cleaving the intermolecular bonds of the chemical network, such as carbon-sulfur (C-S) and/or sulfur-sulfur (S-S) bonds, to shortening of the chains. This process cleaves monosulfidic, disulfidic, and polysulfidic cross-link of vulcanized rubber. The opening of cross-links or the scission of chains can occur by heat and shearing forces. This result is a descent in molecular weight of the polymer. It is likely that thermally generated polymer radicals and hydrogen sulfide and thiol are presented during the thermal degradation [30]. The opening the sulfur cross-links by heat or shearing is shown in Figure 2.5.

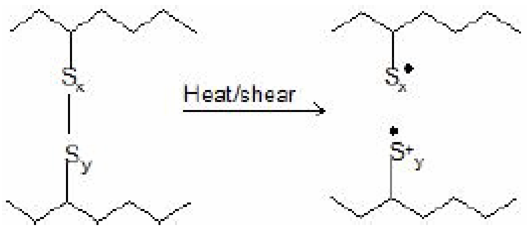


Figure 2.5 The opening the sulfur cross-links by heat or shearing [30].

Reclamation process may be helped by external energy that the three-dimensional network of cross-linked rubber breaks down in presence of different energy sources. The general types of devulcanization method in reclamation are chemical, ultrasonic, microwave, biological, and mechanical method [30-32].

Table 2. 4 General types of devulcanization method [31]

Method	Basic of processing	Zone of reaction
Chemical	Chemicals	Surface of particles
Ultrasonic	Ultrasonic waves	Throughout particles
Microwave	Microwaves	Throughout particles
Biological	Microorganism	Surface of particles
Other	Mechanical steam	Surface of particles

2.2.3.1 Chemical method

Chemical method is based on the use of devulcanizaing agents. Many devulcanizing agents for natural and synthetic rubbers such as diphenyl disulfide, dibenzyl disulfide, diamyl disulfide, butyl mercaptan and thiophenols, xylene thiols, and other mercaptans have been developed. They can selectively break sulfur bonds and are used to dispose the relative amounts of monosulfidic, disulfidic, and polysulfidic crosslinks. Moreover, chemical method is based on use of solvent such as toluene, naphtha, benzene for sulfur vulcanized rubber under high temperature and pressure. The molecular weight of rubber still remains and its microstructure is not significant. However, the process is extremely slow, can be tested only in a small laboratory scale and not be environmental friendly because it involves swelling of the vulcanized rubber in an organic solvent, which may cause pollution and become hazardous. In addition, this process is necessary to separate the devulcanized rubber from solvent. The process is depicted in Figure 2.6.

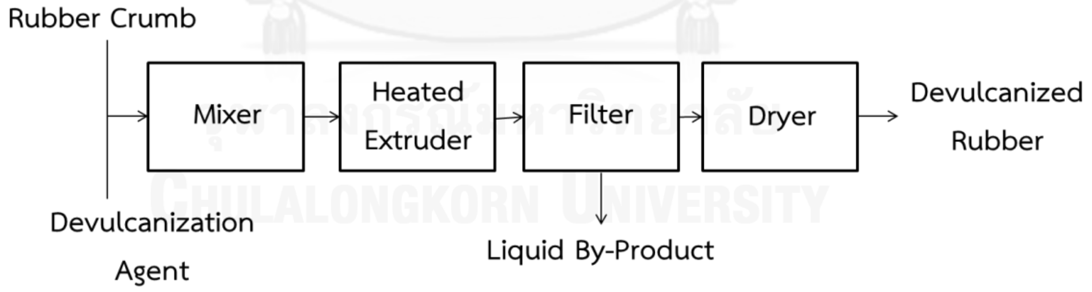


Figure 2.6 Schematic diagram of a chemical devulcanization system [31].

2.2.3.2 Ultrasonic method

The devulcanization process requires a high energy level to break carbon-sulfur and sulfur-sulfur bonds which can be provided by ultrasonic field (Figure 2.7). In this method, solid waste tyre rubbers are immersed into a liquid. Then ultrasonic energy is applied ultrasonic radiation is in the range of about 20 kHz and at a power intensity of larger than 100 watts. Ultrasonic method could break up the main chain bonds and cross-link bonds as independent random advent. An increase in ultrasonic radiation is attended to significant decrease in molecular weight. However, this method requires expensive equipment.

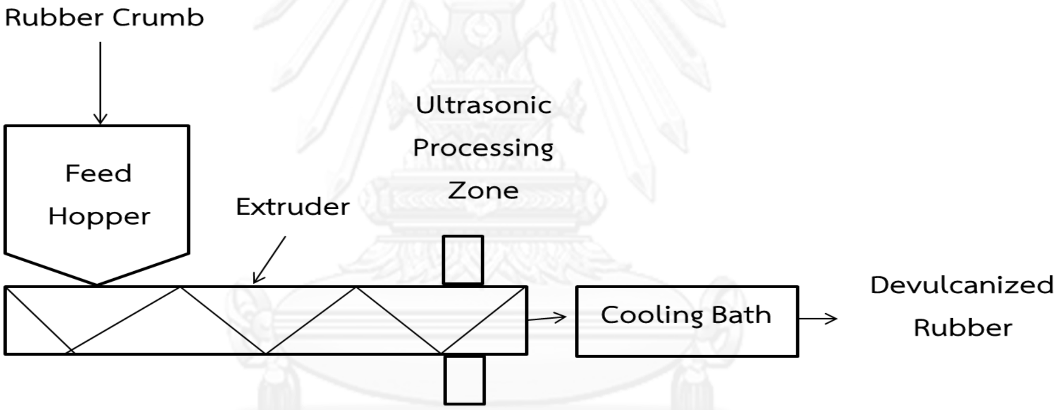


Figure 2.7 Schematic diagram of an ultrasonic devulcanization system [31].

2.2.3.3 Microwave method

In the microwave recycling method (Figure 2.8), the process involves the impregnation of the waste tyre rubber with an essential oil and then treating the material under reduced pressure and radiation. A control dose of microwave electromagnetic energy at specified frequency is used to break the sulfur-sulfur or carbon-carbon bond in the cross-linked rubber. The temperature of the material may increase rapidly to reach finally 260-350 °C. Moreover, microwave energy at 915 or 2450 MHz is sufficient to cleave cross-link bonds but insufficient to cleave polymer chains. The materials for reclamation must have some polarities so that the microwave energy will generate the heat necessary to be devulcanized. Thus, the sulfur vulcanized rubber containing polar groups which is proper for microwave devulcanization. Moreover, carbon black containing rubber is plentiful to ultra-high frequency in a microwave chamber due to ion polarization. This method is very much useful because it is free of solvent and chemical and the process of devulcanization is very fast.

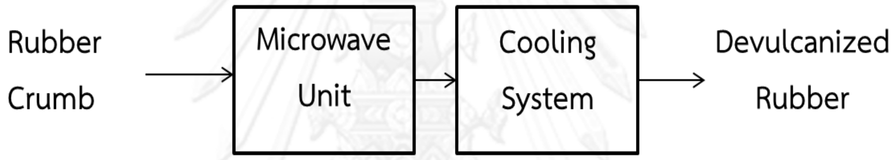


Figure 2.8 Schematic diagram of a microwave devulcanization system [31].

2.2.3.4 Biological method

Biological method by using microorganisms could be to degrade of waste tyre rubber. The process occurred by adaptation of microbial enrichment cultures with tyre rubber for several months that resulted in microbial adaptation to growth on polymeric material and adhesion of co-substrate increase degradation especially for natural rubber. Vulcanized rubber in form of latex is easily degraded while rubbers from used truck tyres are more resistant. Thus, naturally occurring microorganisms are influenced to the environmental conditions and toxicity to chemical compounds in the waste tyre rubber is principal concern. The process is depicted in Figure 2.9.

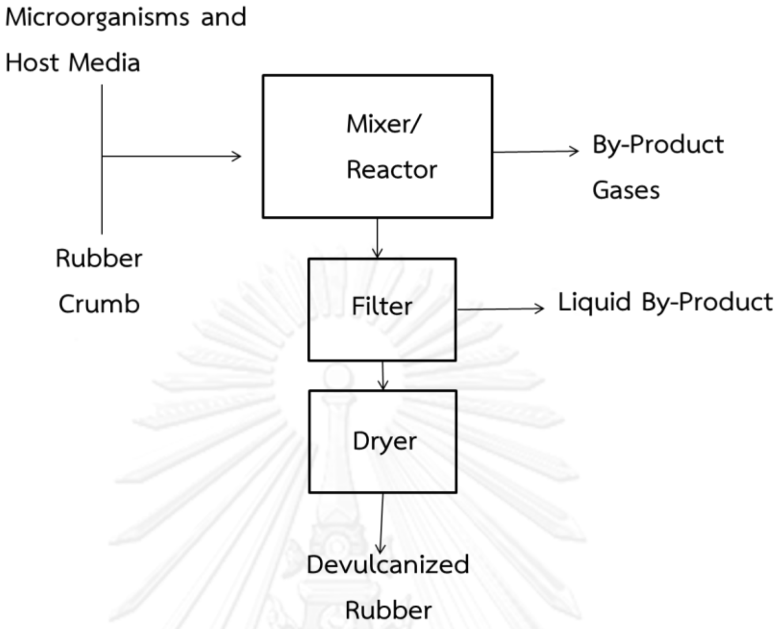


Figure 2.9 Schematic diagram of a biological devulcanization system [31].

2.2.3.5 Mechanical method

Mechanical devulcanization is achieved through the repeated deformation of rubber particles under specific conditions of temperature and pressure. In mechanical reclaiming process, tyre rubber mixed with various reclaiming chemicals and fed into an extruder which rubber is devulcanized at about 200 °C for about 5-10 minutes. In this process, drastic molecular weight breakdown takes place due to mechanical shearing at high temperature.

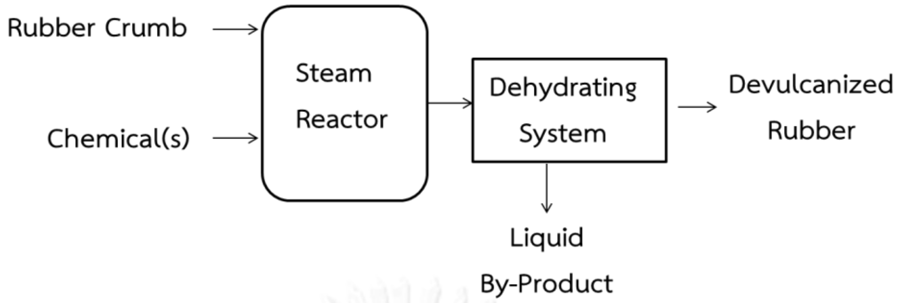


Figure 2.10 Schematic diagram of a mechanical steam devulcanization system [31].

2.3 Cationic polymer

Numerous technologies have been utilized to remove anionic pollutants from aqueous solution such as chemical reduction, adsorption, and microbial remediation. Most conventional methods sometimes suffer from low treatment efficiency and high operation cost. Therefore, the simple process and low cost treatment technologies are still developed to remove anionic pollutants from water. Furthermore, water-soluble polymers are easily available or can be synthesized by different routes and are easy to apply. One group of special cationic polymer is the quaternary ammonium compounds. In previous works, modified polyacrylamides were used as chelating agents for removal of Cu(II), Cd(II), Pb(II), Cr(V), and nitrate ions due to it is a quaternary ammonium salt and has an inherently positive charge on polymer chain [33, 34].

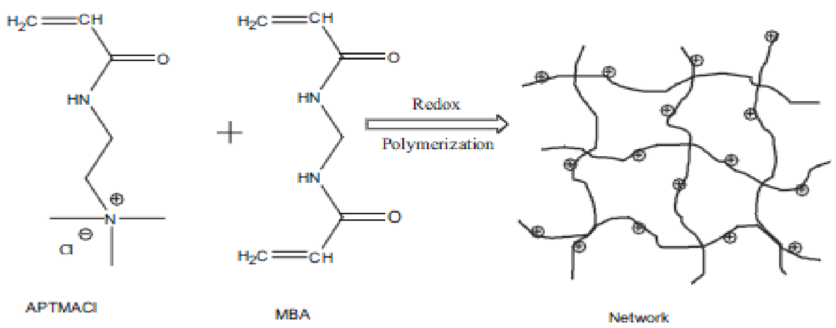


Figure 2.11 Schematic of polymerization of poly(3-acrylamidopropyl)trimethylammonium chloride [35].

Poly(3-acrylamidopropyl)trimethylammonium chloride (p(APTMACl) hydrogels are also interesting smart materials that can develop or have charges of negative and positive, respectively, on ionization and have important in medicine, bioengineering environments, and catalysis application. The p(APTMACl) can be synthesized by free radical polymerization in the presence of (3-acrylamidopropyl)trimethylammonium chloride as a monomer, ammonium persulfate (APS) as redox initiator, *N,N'*-methylenebisacrylamide (MBA) as a cross linker, and *N,N,N',N'*-tetramethylenediamine as an accelerator [35]. Figure 2.11 shows the schematic representation of polymerization those results in three dimensional network formations.

The quaternary ammonium polymer of APTMACl containing chloride has an ability to remove anionic pollutant via anionic exchange between chloride ions and anions and binding these species with the ammonium quaternary cationic group. This bond is assumed through nitrogen of the ammonium group (positively charged) with anions forming a dipole [36].

2.4 Adsorption

Adsorption is the phenomenon of accumulation of materials at the interface between two phases. These phases can be any of the liquid-liquid, liquid-solid, and gas-solid. Adsorption process involves two components adsorbent and adsorbate. The adsorbed solutes are referred to as adsorbate, whereas the solid material is the adsorbent. In the adsorption process, molecules or atom or ions in a gas or liquid diffuse to the surface of solid, where they bond with the solid surface or are held by weak intermolecular forces. In discussing the fundamentals of adsorption, it is useful to understand adsorption isotherms and adsorption kinetics.

2.4.1 Adsorption isotherm

The determining information in understanding the sorption process requires the equilibrium sorption. The adsorption isotherm represents the relationship between the amount adsorbed by a unit weight of solid sorbent and the amount of solute remaining in the solution at equilibrium. The most frequently used isotherms are the Langmuir isotherm and the Freundlich isotherm [37, 38].

Langmuir isotherm explains the monolayer adsorption of adsorbates on homogeneous surface with limited number of active sites and each site can adsorb only one target ion via chemisorption. All sites are energetically equivalent and there is no interaction between the ions. The Langmuir linearized isotherm can be written in equation 2.1.

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \qquad (2.1)$$

where C_e = The equilibrium concentration of adsorbate in the bulk solution (mg/L)

q_e = The amount of adsorbate on the solid at equilibrium (mg/g)

q_m = The maximum adsorption capacity (mg/g)

b = The constant related to the free energy of adsorption (L/mg)

q_m and b can be calculated from the slope and y-axis interception by plotting C_e/q_e versus C_e.

Freundlich isotherm model can be applied to the sorption system which describes the physical sorption of sorbate only, as well as non-ideal sorption on heterogeneous surface with different adsorption energy. The linearized Freundlich equation is shown in equation 2.2.

$$ln q_e = ln K_f + \frac{1}{n} ln C_e \qquad (2.2)$$

where q_e = The amount of adsorbate on the solid at equilibrium (mg/g)

K_f = A constant related to adsorption capacity of the adsorbent $((mg/L)^{1-(1/n)} g^{-1})$

n = Freundlich constant indicating the adsorption intensity

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

By plotting $ln\ q_e$ versus $ln\ C_e$, it gives a linear with a slope of $1/n$ and the interception that is equal to the value of $ln\ K_f$. The slope, $1/n$ is an indicator of adsorption intensity and the intercept, of adsorption capacity.

2.4.2 Adsorption kinetics

The study of adsorption kinetics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. In order to understand better the adsorption behaviors, two kinetic models including pseudo-first order and pseudo-second order are analyzed [39].

The pseudo-first order equation is commonly expressed in linear form as the following equation 2.3.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{2.3}$$

where q_e = The adsorption capacity at equilibrium (mg g^{-1})

q_t = The adsorption capacity at the time t (mg g^{-1})

k_1 = The rate constant of the pseudo-first order adsorption (min^{-1})

The plot of $log\ (q_e - q_t)$ versus t should give a linear correlation from which k_1 and q_e can be determined from the slope and intercept of the plot, respectively.

The pseudo-second order adsorption kinetic rate equation is considered in linear-form as equation 2.4.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{2.4}$$

where q_e = The adsorption capacity at equilibrium (mg g^{-1})

q_t = The adsorption capacity at the time t (mg g^{-1})

k_2 = The rate constant of the pseudo-second order adsorption (g mg^{-1} min^{-1})

The pseudo-second order adsorption kinetic rate can be obtained from a plot of t/q_t against t.

2.5 Literature review

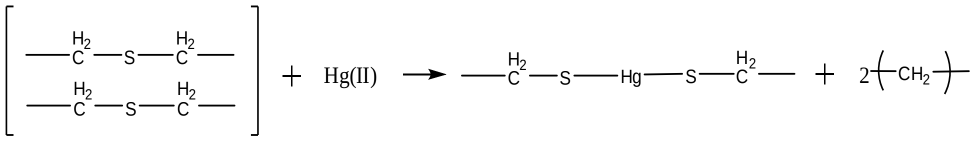
2.5.1 Reuse of waste tyre rubber

As the most waste polymer in the world, waste tyre rubber does not decompose easily due to its cross-linked structure and presence of stabilizers and other additives. Hence, attention is focused on the use of waste tyre rubber as it purposes the problems of managing and into the environment. Waste tyre rubber is a material that is generally used as adsorbent in many fields. This sorbent is an interesting and inexpensive medium for the adsorption of toxic metals from aqueous solutions.

In previous work, waste tyre rubber was used as adsorbent for removal water pollution. Alamo-Nole *et al.* [40] studied the sorption of toluene and xylene by tyre rubber. The adsorption process followed the Freundlich isotherm. The sorbent could remove 60 % of toluene and 81 % of xylene from initial concentration of 50 ppm solutions and attained in the first 30 minutes of contact time by using 5 g/L of adsorbent. The removal of these species occurred through carbon black in tyre rubber, which should promote the removal of dissolved species through adsorption mechanism. Moreover, stearic acid could behave as ionic exchange with metal ions and non-polar organic are expected to interact with the rubber matrix via Van der Waals interaction. Purakayastha *et al.* [41] studied the preparation of adsorbent from waste tyre rubber. The sorbents were washed thoroughly with distilled water, dried at 103 °C for 2 hours and then cooled to room temperature (26 ± 2 °C). The sorbent was then used to remove sodium dodecyl sulfate (SDS) in the solution in batch experiment at pH 6. The adsorption kinetics fixed to the first-order reversible kinetic model and the equilibrium time was found to be 6 hours.

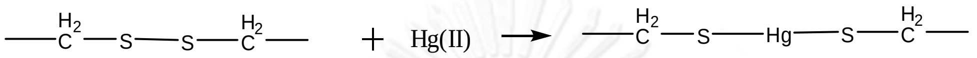
Danwanichakul *et al.* [42] studied the preparation and utilization of the vulcanized rubber as adsorbent to remove mercury (II). The sorbent was shaped a size of 5 mm x 5 mm and 10 mm x 10 mm and then used to remove 5 ppm of mercury (II) in the 20 mL of a stock $HgCl_2$ aqueous solution with various pH (1.81, 7.89, 12.4) and the weight of rubber chips ranged from 0.2 to 1.0 g. Subsequently, to obtain the equilibrium concentration the mixture was shaken for 8 hours at the speed of 160 rpm and at 30 °C. The adsorption kinetics of mercury (II) on the rubber chips followed pseudo-second-order model. In the presence of sulfur atom in cross-link network of the vulcanized rubber, the mercury (II) considered as a soft acid can interact with sulfur groups in the rubber chips as a soft base is highly favorable. The possible reactions could be shown here after.

For monosulfidic crosslink;



$$\left[\begin{array}{c} -\mathrm{CH_2}-\mathrm{S}-\mathrm{CH_2}- \\ -\mathrm{CH_2}-\mathrm{S}-\mathrm{CH_2}- \end{array}\right] + \mathrm{Hg(II)} \rightarrow -\mathrm{CH_2}-\mathrm{S}-\mathrm{Hg}-\mathrm{S}-\mathrm{CH_2}- + 2\left(-\mathrm{CH_2}-\right)$$

For disulfidic crosslink;



$$-\mathrm{CH_2}-\mathrm{S}-\mathrm{S}-\mathrm{CH_2}- + \mathrm{Hg(II)} \rightarrow -\mathrm{CH_2}-\mathrm{S}-\mathrm{Hg}-\mathrm{S}-\mathrm{CH_2}-$$

For polysulfidic crosslink;

$$-\mathrm{CH_2}-\left(\mathrm{S}\right)_n-\mathrm{CH_2}- + \mathrm{Hg(II)} \rightarrow -\mathrm{CH_2}-\mathrm{S}_m-\mathrm{S}-\mathrm{Hg}-\mathrm{S}-\mathrm{S}_{n\text{-}m\text{-}2}-\mathrm{CH_2}-$$

The chips with smaller size yielded higher rate of adsorption and the increasing pH, adsorption affinity of the rubber chip increased.

Calisir *et al.* [8] studied the removal of copper (II) from aqueous solutions by recycled tyre rubber in batch sorption. The weight of 0.1 g ground crumb rubber was used as sorbent and put into 100 mL of copper solution with varying concentration of copper (II) ranging from 1 mg/L to 50 mg/L, varying pH (1.5-7.0), and contact time (6-96 hours). It was shown that the adsorption of copper (II) is pH-dependent and the best results were obtained at a pH of 6.0. The adsorption of copper succeeded and obeyed Langmuir isotherm and involved an ion exchange mechanism by displacement of zinc in the sorbent.

The crosslinking of the polymer main chains during the vulcanization process turns the thermoplastic into a thermoset material which cannot be reshaped by simple heating. In order to break down the cross-linked network, some physical or chemical treatment is necessary. This may also cause surface modification in tyre rubber components, having a favorable effect on the adsorption behavior. Zanchet *et al.* [43] studied devulcanization of rubber by microwave method. The results showed the increasing temperature of waste tyre rubber with increased exposure time of microwave radiation (100 g of styrene-butadiene rubber, 100 watts of microwave radiation, speed of 40 rpm). The higher temperature caused devulcanization process or cleavage of carbon to carbon and sulfur to sulfur bonds. Gupta *et al.* [44] synthesized rubber tyre activated carbon (RTAC) from waste tyre rubber for removal of lead and nickel ions from aqueous solutions. They prepared the adsorbent by carbonizing tyre rubber at 500 °C for 5 hours. Then, the adsorbent was treated with hydrogen peroxide solution for 24 hours at 60 °C to oxidize organic impurities and washed with deionized water and dried at 110 °C for 2 hours. After that, the adsorbent was activated to 900 °C for 2 hours, treated with HCl solution and drying at 100 °C for 24 hours. The adsorption study of lead and nickel ions was investigated under various conditions; pH 2-8, contact time (10-270 minutes), temperatures (298, 308, 318 K) for varying initial concentration (20 - 200 ppm). It was shown the adsorption followed the Langmuir isotherm and the pseudo-second-order model for the kinetics study due to the fact that higher meso-porosity has a significant enhance the adsorption capacity of RTAC for liquid phase adsorption of lead and nickel removal. Alexandre-Franco *et al.* [45] studied adsorption of cadmium by modified waste tyre rubber in batch method. Tyre rubber was treated at 400-900 °C for 2 hours under N_2 and at 850 °C for 2 hours in steam. Then, the adsorption process of cadmium was studied by using 0.1 g of adsorbent at various pH (2.3-9.0), and contact time (15 minutes – 360 hours) at initial concentration of cadmium at 4.6

x 10^{-3} M. This study showed the adsorption followed the pseudo-second order kinetic model and the process depended on the pH, being the larger at pH 4.6 or 7.0.

2.5.2 Arsenic removal by adsorption

Contamination of water due to arsenic is a concern problem. Many present investigation purpose to remove arsenic. Singh and Pant [46] studied adsorption of arsenite (As(III)) on activated alumina. Batch adsorption experiments were carried out by shaking 1 g of activated alumina with 100 mL aqueous solution of arsenite with initial concentrations of 0.5 and 1.5 ppm. The adsorption experiments were well fit to both Freundlich and Langmuir adsorption isotherms. It was shown that activated alumina had high affinity towards As(III) ions at pH 7 and kinetics of As(III) was very rapid in the first 6 hours. Moreover, the removal of arsenate and arsenite was studied by using reclaimed iron-oxide coated sands (IOCS) by Hsu *et al.* [47]. The batch experiments were studied by using various IOCS dosages (4 - 24 g/L), arsenate and arsenite initial concentrations ranging from 10-500 ppm and the initial solution pH ranging from 5 to 8 were investigated. The results showed that when the adsorbent dosage and initial arsenic concentration were fixed, both the arsenate and arsenite removals decreased with increasing initial solution pH. The adsorption isotherms of arsenate and arsenite fitted the Langmuir isotherm model and the removal efficiencies of total arsenic were in order As(V) > As(V) + As(III) > As(III). Habudo-Stanic *et al.* [48] used natural alum silicate exchanger, zeolite clinoptilolite and ionic exchanger Dowex Marathon C with hydrous ferric oxide for removal of arsenite and arsenate. The adsorbents were saturated with Fe^{3+} ions from $FeCl_3$ solution in acetate buffer solution (pH 3.6) and converted to hydrous oxide by NaOH and NaCl at 50 °C. Adsorption kinetics of arsenic was studied of initial arsenic concentrations ranging from 100 to 500 ppm, contact time from 15 to 360 minutes and pH at 6.4, 6.9, 7.4, and 7.9 with using 0.25 g adsorbents. It was shown that the adsorption percentage of arsenite ions increased with the increase of pH with maximum at pH 7.4 and contact time but increase of the initial concentration had no significant effect on the arsenite adsorption. While, the adsorption percentage of arsenate increased with the increase of contact time but the increase of pH and initial concentration resulted in the decrease of the arsenate adsorbed and maximum arsenate adsorption was achieved at pH 6.4.

Moreover, it is well known that arsenite has an especially high affinity for tissue proteins by strongly binding to mercaptan (thiol) groups, hence, Hao *et al.* [49] studied the preparation inorganic-organic hybrid adsorbents bearing thiol groups which prepared by modifying activated alumina (AA) for removal of arsenite from water. The batch adsorption tests were investigated by using 0.1 g of adsorbent added into 100 mL of arsenic solution with the desired initial concentration (2-20 ppm) at pH 7.0 and shaken at room temperature. The adsorption showed the increasing uptake of arsenite when the thiol loading increased. Furthermore, Barakat and Sahiner [35] studied the removal of arsenate from aqueous medium by synthesizing poly(3-acrylamidopropyl)trimethylammonium chloride (p(APTMACl)) hydrogel. The adsorption experiments were investigated in a pyrex glass flask containing 500 mL of arsenate solution with different amounts of hydrogels. The adsorption experiments were carried out for 360 minutes. The results demonstrated a removal efficiency of approximately 99.7 % by immersing 1.5 g hydrogel/L in a solution containing 50 ppm arsenate at pH 9 for 360 minutes. Aslam Malana *et al.*[50] used a composite of nano ferrite with polymer (methyl acrylate, vinyl acetate, acrylic acid) as adsorbent for the arsenic removal at pH 6. Adsorption studies of arsenic were studied of different concentrations (20 – 200 ppb) by shaking at 313 K, contact time of 90 minutes with using 0.05 g of adsorbent. It was shown that the equilibrium data was fitted to Freundlich model and the maximum adsorption capacity (q_m) of arsenic on the adsorbent was found to be 0.053 mg/g. Santos *et al.*[51] studied adsorption of arsenate on the iron-PVA hydrogel microspheres. Batch adsorption experiments were carried out by using 0.175 g of sorbent with 50 mL aqueous solution of arsenate with initial concentrations of 92.90 mg/L. Maximum arsenate adsorption was found to be 87.18 mg/g at contact time 4 hours and the pH range of 2-5, in accordance with the Langmuir model. The sorbent can be used in fixed bed columns, reaching and adsorptive capacity of 28.65 mg As(V)/g. Sahiner *et al*. [52] prepared modifiable bulk and nanogels based on 4-vinylpyridine quaternized with HCl (p(4-VP)-HCl). It was shown that p(4-VP)-HCl removed over 95% of As(V) in 15 minutes whereas bulk hydrogels removed over 82% of the As(V) in 12 hours.

In this work, we aimed to improve the efficiency of arsenic removal in solution by using surface-modified waste tyre rubber powder and by cationic polymer in order to enhance its arsenic extraction efficiency.

CHAPTER III

EXPERIMENTAL

3.1 Analytical instruments

Table 3.1 Instruments list

Instruments	Model, Manufacturer
Inductively coupled plasma optical emission spectrometer	iCAP 6500, Thermo Scientific
Particle size analyzer	Malvern Mastersizer
Fourier transforms infrared spectrometer	NICOLET 6700, Thermo Scientific
Balance	SI-234 DENVER
Oven	Memmert
pH meter	Ultrabasic, DENVER
Stirrer	Gem: MS101
Shaker	Model HS 500 (Janke & Kunkel)
Sonicator	CREST
Microwave	SHARP, R-362

3.2 Chemicals

Table 3.2 Chemicals list

Chemicals	Supplier
Waste tyre rubber powder	Union Commercial Development Co. Ltd.
D-limonene	Sigma-Aldrich

Table 3.2 Chemicals list (continued)

Chemicals	Supplier
Triton X-100	Fluka/AR
(3-Acrylamidopropyl)trimethylammonium chloride (75 w% solution in water) (APTMACl)	Sigma-Aldrich
N,N”-methylene bisacrylamide (MBA)	Sigma-Aldrich
N,N,N’,N’-tetramethylethylenediamine (TEMED)	Sigma-Aldrich
Ammonium persulfate (APS)	Sigma-Aldrich
The stock solution of 1000 mg As(V)/L	Sigma-Aldrich
The stock solution of 1000 mg As(III)/L	Sigma-Aldrich
Hydrochloric acid	Merck
Sodium hydroxide	Merck

3.3 Preparation and modification of adsorbent

3.3.1 Reclamation of waste tyre rubber

Waste tyre rubber (WTR) powder, the raw material in this work, was obtained from Union Commercial Development Co. Ltd. (Samut Prakan, Thailand). Reclamation method was applied from U.S. Patent 5362759 [53]. About 0.50 g of WTR was mixed with 5% of D-limonene and 50 µL of Triton X-100. Then, the mixture was dried in an oven at 80 °C for 10 hours. After that, the mixture was taken in the microwave oven for the reclamation by microwave radiation at 1100 watts for 2, 5, 10 and 15 minutes. The WTR before and after each reclamation period was characterized by Fourier transforms infrared spectroscopy (FT-IR, NICOLET 6700, Thermo Scientific).

3.3.2 Modification of waste tyre rubber

WTR (non-reclaimed and reclaimed) was surface-modified with (3-acrylamidopropyl)trimethylammonium chloride (APTMACl) in order to enhance its arsenic adsorption efficiency. Approximately 0.50 g of WTR was mixed with 5 mL of desired amounts of APTMACl monomer with varying concentrations in the range of 250 to 2000 mM, 10 mM of TEMED and 50 mM of MBA. Then, the mixture was sonicated for 15 minutes and purged by N_2 for 1 hour. About 0.50 mL of 70 mM APS was added to initiate polymerization reaction and stirred continuously for 1 hour to complete the reaction. The solid was afterwards separated by filtration. After that, it was washed twice with 5 mL of deionized water and dried at 50 °C for 24 hours and kept for further use.

3.4 Characterization of waste tyre rubber

3.4.1 Particle size distribution

The morphological characteristic of waste tyre rubber before and after reclamation by microwave method was characterized by using a Malvern Mastersizer particle size analyzer, which utilizes the principle of laser ensemble light scattering.

3.4.2 Fourier transforms infrared spectroscopy

The functional groups on the surface of the waste tyre rubber and the resulting modified-waste tyre rubber by reclamation with microwave method and by modification of poly(3-acrylamidopropyl)trimethylammonium chloride (p(APTMACl)) were resolved by FT-IR analysis (NICOLET 6700, Thermo Scientific). The FT-IR spectrum was recorded in the range of 4000 to 400 cm^{-1} in attenuated total reflectance (ATR) mode.

3.5 Batch extraction

3.5.1 Arsenic extraction capacity of p(APTMACl)-modified waste tyre rubber

To compare the arsenic extraction efficiency of the non-reclaimed waste tyre rubber and the p(APTMACl)-modified waste tyre rubber (WTR/p(APTMACl)), the batch extraction technique was used. A mass of 0.10 g of adsorbent was added into 10 mL of standard solution of 10 mg/L As(III) or As(V) in a test tube under shaking at room temperature for 24 hours. Then, the suspension was filtered through a 0.45 μm filter membrane. The arsenic concentrations in the solution before and after the extraction at each experiment were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES). All experiments were performed in triplicate (n=3). From the obtained results, the adsorption efficiency of arsenic extraction was calculated using Equation 3.1.

$$q = \frac{(C_o - C_f)}{w} V \qquad (3.1)$$

where q is the adsorbed amount of arsenic onto the adsorbent (mg/g)

C_o is the initial arsenic concentration in solution (mg/L)

C_f is the final arsenic concentration in solution (mg/L)

V is the volume of arsenic solution (L)

W is the weight of adsorbent (g)

3.5.2 Effect of pH

In this experiment, the effect of pH of the arsenic solution was studied so as to determine the optimum pH range for maximum arsenic adsorption. The effect of pH was studied in the pH rang of 3.0 to 10.0 by using 1%(v/v) HCl and 1%(w/v) NaOH solution for pH adjustment. Ten milliliters of arsenic standard solution with the concentration of 10 mg/L and 0.10 g of adsorbent were shaken in a test tube for 24 hours at room temperature and the solid was separated by filtration. The amount of arsenic before and after extraction at each assay was determined by ICP-OES. After that, the arsenic extraction efficiency (*q*) of each system was calculated similarly to the previous section.

3.5.3 Effect of concentration of APTMACl

The effect of (3-acrylamidopropyl)trimethylammonium chloride (APTMACl) was investigated to determine the optimum loading to waste tyre rubber for arsenic extraction. Approximately 0.50 g of WTR was mixed with 5 mL of the varying concentration of APTMACl in the range of 250 to 2000 mM and 10, 50 mM of TEMED and MBA, respectively. The mixture was sonicated for 15 minutes and purged by N_2 for 1 hour. After that, 0.50 mL of 70 mM APS was added and stirred for 1 hour. The sorbents were washed twice with 5 mL of deionize water, dried at 50 °C for 24 hours and kept for the further use.

Approximately 0.10 g of adsorbents were added into a test tube containing 10 mL of arsenic standard solution of 10 mg/L and shaken for 24 hours at room temperature. The solid was separated by filtration and the amount of arsenic was determined by ICP-OES. The arsenic extraction efficiency (*q*) was calculated according to Equation 3.1.

3.5.4 Effect of drying temperature of adsorbents

The drying temperature of WTR/p(APTMACl) adsorbent was typically influenced to enhance the ability of arsenic extraction. This experiment was also carried out to investigate effect at a relatively higher temperature. About 0.50 g of WTR was mixed with 5 mL of desired amount of APTMACl and 10 mM, 50 mM of TEMED and MBA, respectively. The mixture was sonicated 15 minutes; purged by N_2 1 hour and 0.50 mL of 70 mM APS was added. The suspension was stirred for 1 hour, felted and washed twice with 5 mL deionize water. The adsorbent was dried at 50 and 100 ℃ for 24 hours.

The effect of drying temperature of WTR/p(APTMACl) adsorbent between 50 and 100 ℃ on the extraction of arsenic was investigated for initial concentration of 10 mL arsenic solution of 10 mg/L at optimum pH and contact time of 24 hours. The arsenic concentration in the solution before and after the extraction was resolved by ICP-OES. The changing in arsenic solution was calculated to the arsenic extraction efficiency (*q*) as expressed in the Equation 3.1.

3.5.5 Adsorption isotherm

Under the optimum conditions, the WTR/p(APTMACl) adsorbent of optimum concentration of APTMACl and drying temperature of adsorbent from the previous studied was used to study the adsorption of arsenic on the surface of adsorbent by the adsorption isotherm. About 0.10 g of WTR/p(APTMACl) was added into 10 mL of various initial concentration of arsenic solution in the range of 5 to 60 mg/L with optimal pH. The mixture was shaken at room temperature for 24 hours to ensure of the adsorption equilibrium. The solid was separated by filtration. The residual arsenic concentrations in each solution were then determined by ICP-OES and the Langmuir and Freundlich models were studied.

3.5.6 Effect of contact time

This experiment purposes to assay the contact time of arsenic solution onto the surface of WTR/p(APTMACl) adsorbents. 0.10 g of WTR/p(APTMACl) was added into 10 mL of 10 mg/L of arsenic solution with the optimum pH value. The mixture was shaken at room temperature for 30 to 360 minutes. The residues were separated by filtration and the filtrates were analyzed for arsenic concentration by ICP-OES. Finally, the arsenic extraction efficiency and kinetic adsorptions were studied.

3.6 Column extraction

Experiments using cylinder column were conducted to investigate the arsenic extraction performance of the developed sorbent. Wastewater was fed through a column packed with appropriate amount of adsorbent under continuous flown condition. The cylinder columns were applied to investigate the arsenic extraction as show in Figure 3.1.

Figure 3.1 Photograph of cylinder column extraction setup.

3.6.1 Effect of flow rate

WTR/p(APTMACl) adsorbents which prepared under the optimal conditions from the previous studies were packed into a home-made cylinder column (syringe plastic volume of 5 mL, id 12.46 mm). The heights of columns were 1 cm, 1.5 cm, and 2 cm. For the studies with different heights of the column, the actual flow rates of the solution passing through column were pre-calibrated with deionized water. Therefore, an aqueous solution containing 25 mL of 10 mg/L arsenic was passed through the column at different flow rates. Finally, the eluate was analyzed for arsenic adsorption efficiency by ICP-OES.

3.6.2 Desorption of adsorbents

Desorption of adsorbents was studied by using the leaching solutions, which were 0.05 M, 0.1 M, and 0.5 M HCl. Each experiment consisted of adding 25 mL of the leaching solution into the column packed with WTR/p(APTMACl) which previously adsorbed arsenic at the optimum flow rate. This experiment was investigated at room temperature and the arsenic concentration before and after desorbed was determined by ICP-OES.

3.6.3 Breakthrough curve

To determine the adsorption capacity of this method, the arsenite and arsenate extraction efficiency of the WTR/p(APTMACl) adsorbent were compared. The cylinder column packed with an appropriate height of WTR/p(APTMACl) and optimum flow rate and pH was prepared from the previous studied. The volume of arsenic solutions was varied in the range of 10 to 120 mL. Each 10 mL arsenic solution of 10 mg/L was passed through the cylinder column. After that, the residual arsenic concentration of the eluate solution was determined by ICP-OES.

3.7 Arsenic extraction from industrial wastewater

Two industrial wastewaters in this work were provided by PTT Public Company Limited. Both of these wastewaters contained some suspended particles, so they were filtered before being used. Twenty-five milliliters of each wastewater were consecutively passed through the cylinder column with appropriate amount of adsorbent and flow rate from the previous studied. The arsenic concentrations in the solutions were determined by ICP-OES.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Preparation and modification of adsorbent

4.1.1 Reclamation of waste tyre rubber

The waste tyre rubber powder used in this experiment was dark solid. After undergoing the reclamation process by microwave method with various exposure times, this material was heated and the explosion at 5.48 minutes occurred and the burnt WTR powder was shown in Figure 4.1 (C). Furthermore, the waste tyre rubber which containing D-limonene and Triton X-100 for the reclamation process, was also heated and the softness increased with the increasing exposure time as shown in Figure 4.2.

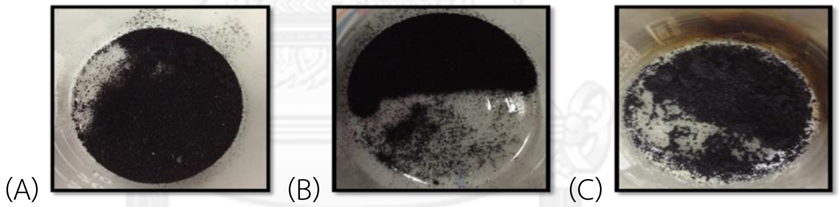


Figure 4.1 Appearance of WTR after reclamation at (A) 2 minutes, (B) 5 minutes, (C) 5.48 minutes.

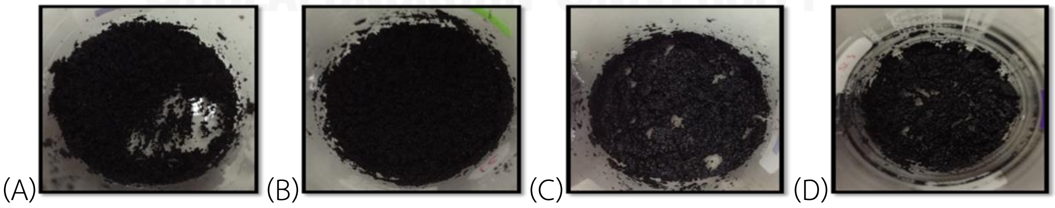


Figure 4.2 Appearance of WTR containing D-limonene and Triton X-100 after reclamation at (A) 2 minutes, (B) 5 minutes, (C) 10 minutes, (D) 15 minutes.

It is well known that the different particle size distribution has different properties; the surface area is prospered to increase with decreasing particle size. Therefore, to compare the particle size distribution of WTR and WTR reclaimed at 5 minutes, particle size distribution analysis was used.

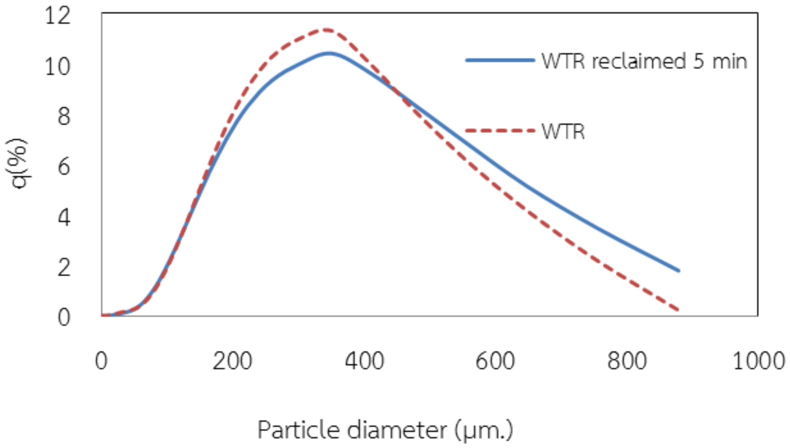


Figure 4.3 Particle diameter of WTR and WTR reclaimed at 5 minutes.

Particle size parameters of non-reclaimed WTR and WTR reclaimed by microwave method at 5 minutes samples are shown in Figure 4.3. The mean particle size distribution of original WTR and WTR reclaimed at heating time 5 minutes are 295 and 315 μm. The data showed that the non-reclaimed WTR contained finer particles than the WTR reclaimed 5 minutes. The reason is that the WTR consisted originally of tiny, small and large sizes, after being reclaimed by heat and microwave exposure the tiny WTR particles could be burnt and decomposed. But this heat was not enough to destroy small and large WTR particles, thus the reclaimed WTR composed of larger particles than the original one. This assumption was in accordance with the result of particle size distribution analysis shown in Figure 4.3.

Moreover, the heating from microwave method may cause the aggregation of particles. The aggregation of the particles during the reclaiming process might be caused by heat resulting that the WTR particles could possibly attached together. It would be resulted that WTR reclaimed at 5 minutes contained bigger particles than non-reclaimed WTR. The FT-IR spectra in ATR mode of the original WTR, reclaimed WTR, and WTR containing D-limonene and Triton X-100 reclaimed by microwave method are illustrated in Figures 4.4 and 4.5, respectively.

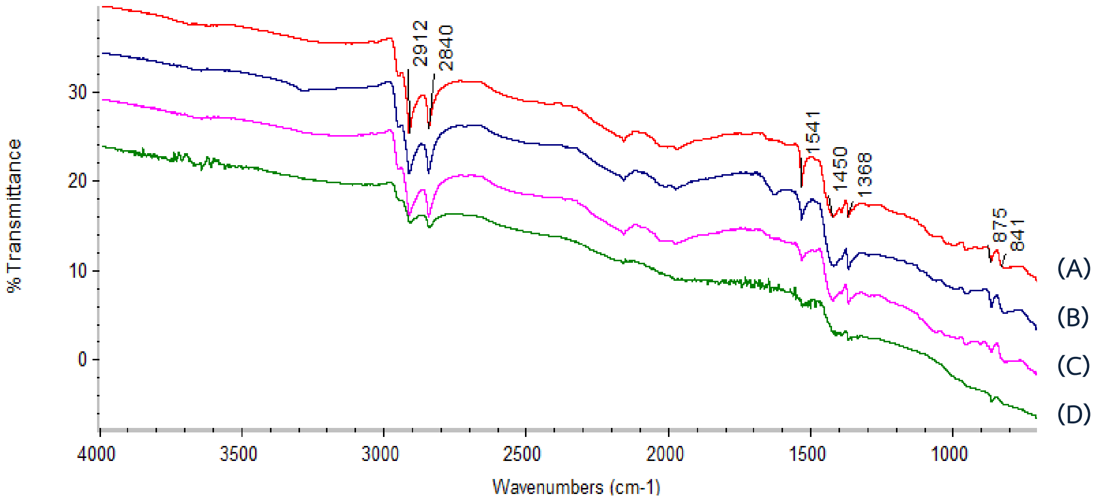


Figure 4.4 FT-IR spectra of (A) WTR, (B) WTR reclaimed 2 minutes, (C) WTR reclaimed 5 minutes, (D) WTR reclaimed 5.48 minutes.

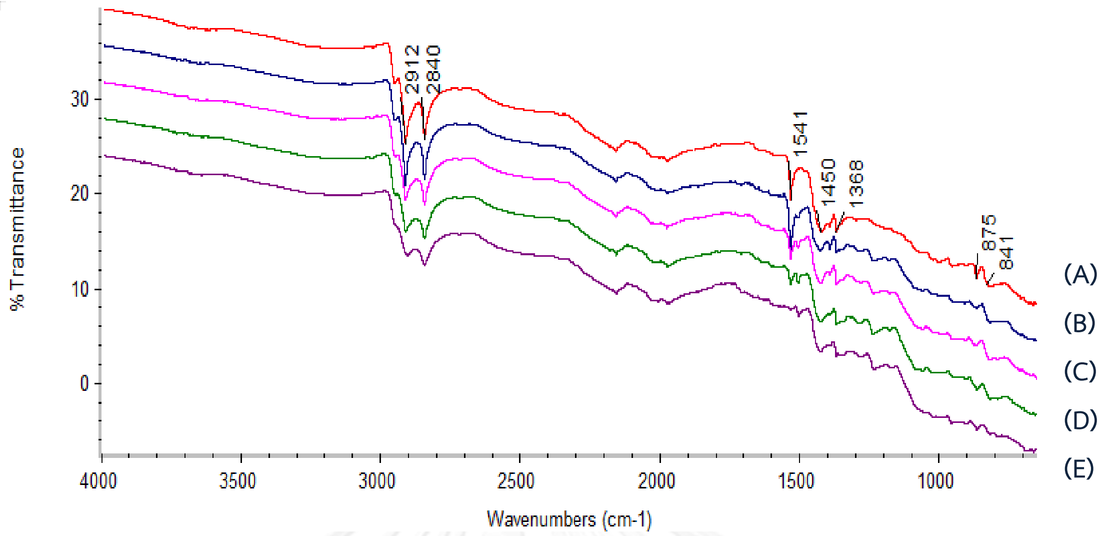


Figure 4.5 FT-IR spectra of (A) WTR, (B) WTR/D-limonene, Triton X-100 reclaimed 2 minutes, (C) WTR/D-limonene, Triton X-100 reclaimed 5 minutes, (D) WTR/D-limonene, Triton X-100 reclaimed 10 minutes, (E) WTR/D-limonene, Triton X-100 reclaimed 15 minutes.

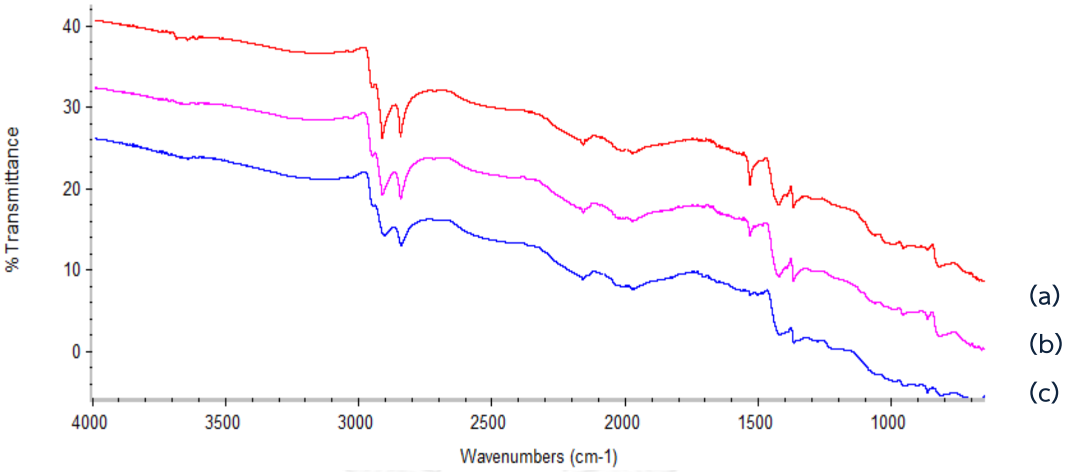
From the Figure 4.4 and 4.5, the peaks in the region 2912 and 2840 cm^{-1}, as well as the peaks between 1450 and 1368 cm^{-1}, are assigned to the CH_3 and CH_2 bonds and the peak at 1541 cm^{-1} is assigned to the COO^- stretching of zinc carboxylates, relative to the rubber structure [43]. The small peaks occurring at 875 and 841 cm^{-1} are due to $–CH_2$-S- groups of the rubber structure for all types of WTR [54].

In general, thermal-treatment presented a more pronounced change in the chemical structure of the elastomers, related to the degradation of the rubber chain during microwave exposure. These changes were evidenced by the decrease in the intensity of peaks. These peaks indicated that the WTR and WTR containing D-limonene and Triton X-100 presented a more pronounced change in its chemical structure with increase the microwave exposure time in Figures 4.4 and 4.5. It is possible that with the increase of exposure time, promoting higher main chain and cross-linked scission of the rubber matrix. In this case, the WTR reclaimed at 5 minutes and WTR containing D-limonene and Triton X-100 reclaimed at 15 minutes were more prone to be devulcanized by microwave method, resulting in use to modification with cationic polymer to increase its arsenic-binding efficiency.

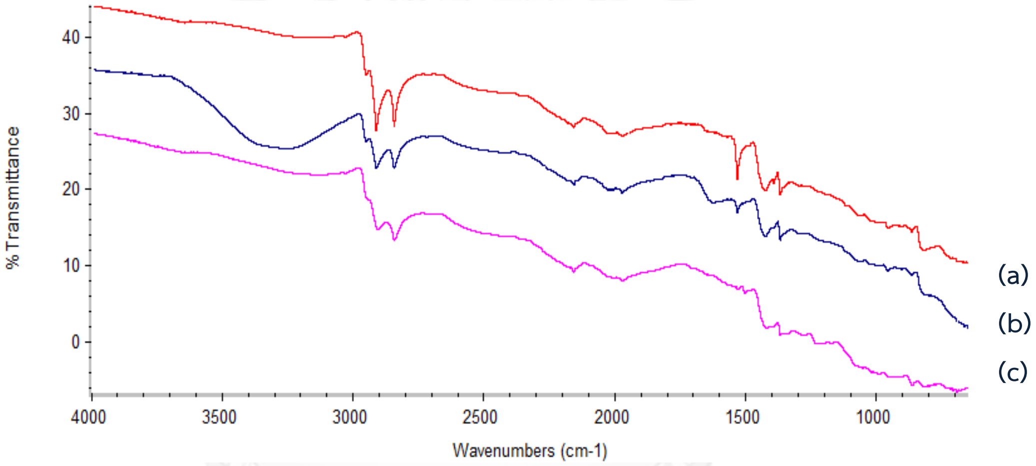
4.1.2 Modification of waste tyre rubber

In order to enhance arsenic extraction efficiency, WTR, WTR reclaimed at 5 minutes and WTR containing D-limonene and Triton X-100 reclaimed at 15 minutes were modified with poly(3-acrylamidopropyl)trimethylammonium chloride (p(APTMACl)). Approximately 0.50 g of WTR was mixed with desired amounts of APTMACl, TEMED, and MBA. The mixture was sonicated for 15 minutes and purged by N_2 for 1 hour. The solid was separated by filtration, washed twice with 5 mL of deionized water and dried at 50 °C for 24 hours.

To determine the optimum concentration of APTMACl monomer between 500 and 1000 mM and the effect of cross linker (MBA), four conditions were studied as illustration in Figures 4.6 and 4.7.



(A) 500 mM of APTMACl

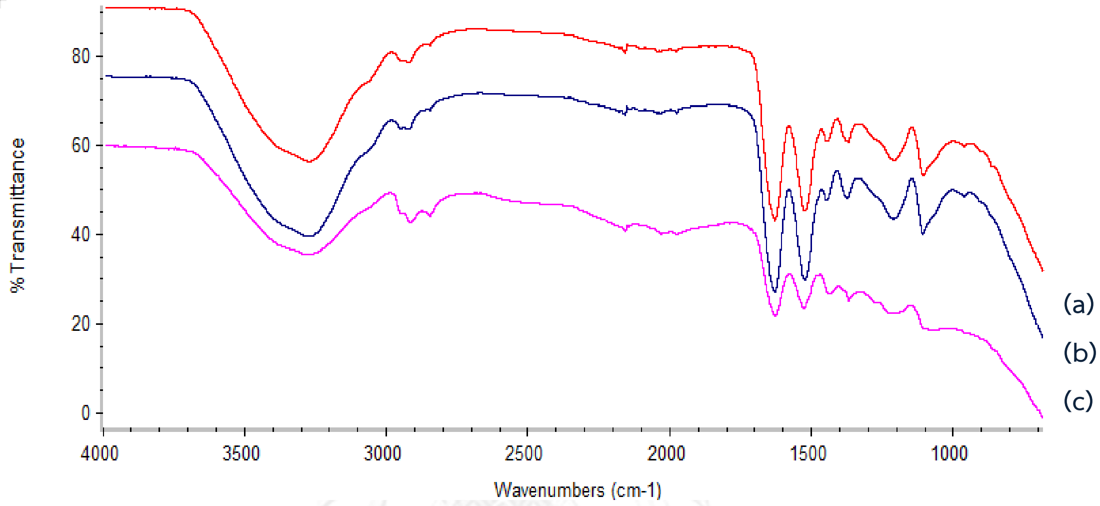


1000 mM of APTMACl

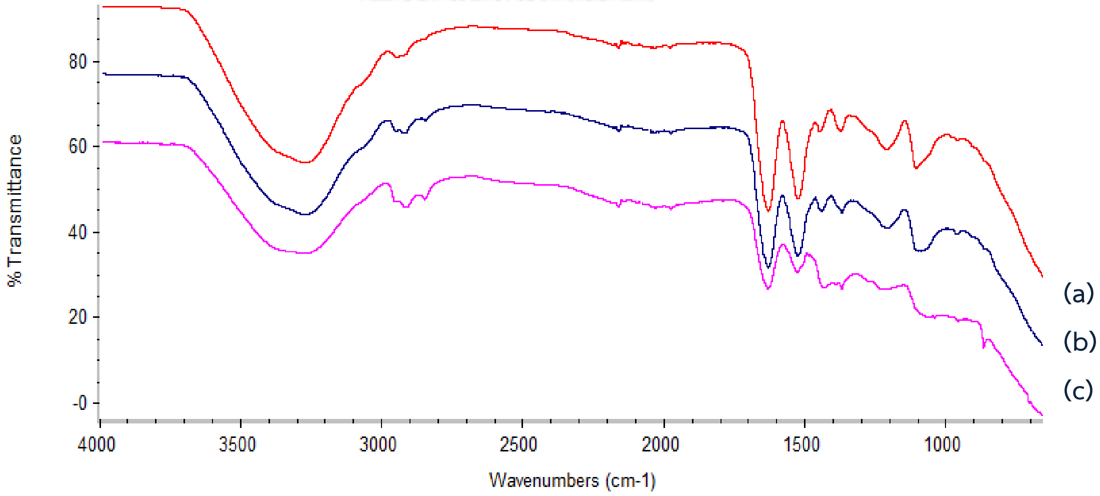
Figure 4.6 The spectra of (a) WTR, (b) WTR reclaimed 5 minutes, (c) WTR containing D-limonene and Triton X-100 reclaimed 15 minutes with no MBA (A) 500 mM APTMACl, (B) 1000 mM APTMACl.

The characteristic peaks at 2840 and 2912 cm^{-1} are assigned to the CH_3 and CH_2 bond and the bands at 1354, 1421, and 1536 cm^{-1} attributed to the amine groups [33, 43] of which p(APTMACl) were also noticed in WTR and WTR containing D-limonene and Triton X-100 both of 500 and 1000 mM of APTMACl (Figure 4.6 A and

B). The addition of crosslinker MBA in the adsorbents influenced to chemical structure as shown in Figure 4.7 (A) 500 mM APTMACl, (B) 1000 mM APTMACl with 50 mM MBA.



(A) 500 mM of APTMACl



(B) 1000 mM of APTMACl

Figure 4.7 The spectra of (a) WTR, (b) WTR reclaimed 5 minutes, (c) WTR containing D-limonene and Triton X-100 reclaimed 15 minutes with MBA (A) 500 mM APTMACl, (B) 1000 mM APTMACl.

The characteristic peaks at 3200-3400 cm^{-1} due to OH were observed in Figure 4.7(A) and (B). It was possibly caused by the chemical reaction between water and polymer matrix as previous polymerization process. In addition, the increase of the peaks at 1210, 1368, 1531, and 1632 cm^{-1} corresponding to the amine bond (-NH) [33, 54] of polymer in adsorbent were detected. The intensity of these peaks of WTR and WTR reclaimed at 5 minutes was higher than WTR containing D-limonene and Triton X-100 reclaimed at 15 minutes for both of 500 and 1000 mM APTMACl as shown in Figure 4.7(A) and (B), respectively. It was possible that the addition of D-limonene and Triton X-100 in the WTR for microwave method did not enhance the polymerization and attachment of p(APTMACl) on the WTR surface. These peaks confirmed that MBA crosslinker was more suitable to enhance the loading of p(APTMACl) onto WTR.

Moreover, the chemical structure of adsorbent with using 500 mM APTMACl (Figure 4.7(A)) was similar to 1000 mM APTMACl (Figure 4.7(B)). It was believed that the 500 mM APTAMCl was still partially polymerized and coated onto WTR adsorbents. Therefore, the results demonstrated that WTR and WTR reclaimed at 5 minutes and polymerized with p(APTMACl) using 500 mM APTMACl and MBA possessed great intensity of amine bond in monomer and crosslinker which was possible to enhance arsenic adsorption efficiency.

4.2 Batch extraction

4.2.1 Arsenic extraction capacity of the p(APTMACl)-modified waste tyre rubber

To compare the arsenate extraction efficiency by original WTR, WTR/p(APTMACl) and WTR reclaimed at 5 minutes/p(APTMACl), 0.1 g of sorbents were put into a solution of 10 mg/L As (V) 10 mL, with initial pH controlled at 3-10. As a result, the As(V) extraction efficiency by original WTR was almost similar at all initial pH (Figure 4.8). At pH 6, WTR showed the higher adsorption amount of 0.054 mg/g. Therefore, the solution pH 6 was also used for investigating As(V) extraction by WTR/p(APTMACl) and WTR reclaimed at 5 minutes/p(APTMACl). Experimental results showing As(V) extraction at the solution pH 6 are presented in Table 4.1.

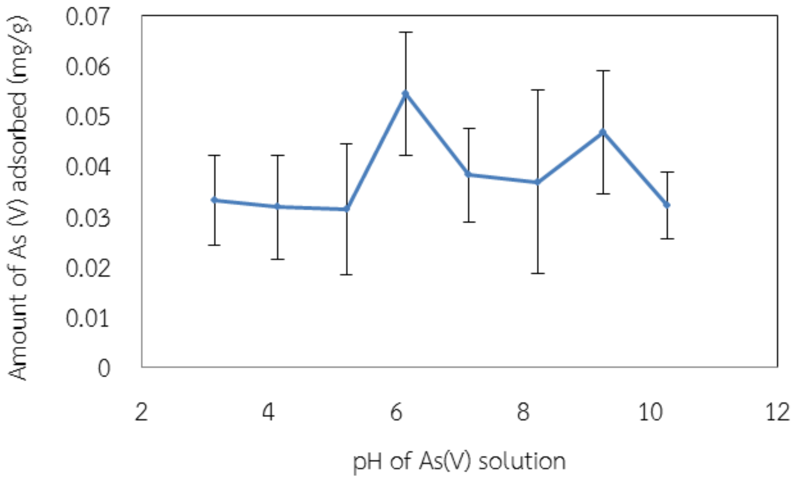


Figure 4.8 Effect of pH on As(V) adsorption by WTR (initial concentration = 10 mg/L (10 mL); adsorption time = 24 h; adsorbent = 0.1 g).

Table 4.1 As(V) extraction efficiency by WTR, WTR/p(APTMACl), WTR reclaimed at 5 minutes/p(APTAMACl) at solution pH 6

Adsorbent	Extraction of As(V) (mg/g)
WTR	0.05 ± 0.01
WTR/p(APTMACl)	0.23 ± 0.01
WTR reclaimed at 5 minutes/p(APTAMCl)	0.03 ± 0.08

Obviously, the enhancement of As(V) extraction by WTR/p(APTMACl) was higher than WTR and WTR reclaimed at 5 minutes/p(APTMACl). It was possible that the reclamation WTR by microwave method did not enhance the coating of p(APTMACl) onto the WTR. In addition, carbon black, stearic acid and sulfur in the form of thiol groups and polysulfide links in WTR could also behave as an ionic exchanger [7, 40]. Furthermore, due to the large available surface areas of p(APTMACl), As(V) would be entrapped onto the polymer by electrostatic attraction or van der Waals force. In addition, WTR/p(APTMACl) adsorbent contains the functional group of trimethylammonium $-N^{+}(CH_3)_3$ that carries a permanent positive charge, which is highly susceptible to ion exchange during the process of adsorbing the anion species [11]. It was expected that the trimethylammonium group would provide the major adsorption sites. The amide group, existing both in the monomer and cross linker (MBA), is also susceptible to arsenate adsorption. As chloride is initially attached to the $-N^{+}(CH_3)_3$ group for charge balance, in the presence of arsenate species, the exchange between anions might occur during the process of adsorption, in which the mechanism should be ion exchange. Therefore, in this study, WTR/p(APTMACl) was more proper to the extraction of arsenic for the further experiments.

4.2.2 Effect of pH

The adsorption amount of WTR/p(APTMACl) was evaluated by using As(III) and As(V) solution (10 mg/L) in the pH range of 3-10 with the adsorption time of 24 hours.

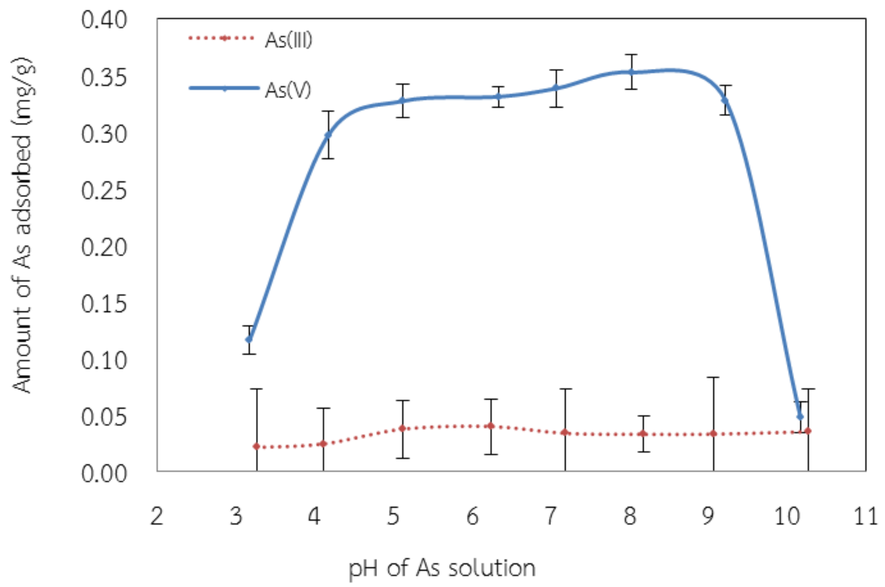


Figure 4.9 Effect of pH on As(III), As(V) adsorption (initial concentration = 10 mg/L (10 mL); adsorption time = 24 h; adsorbent = 0.1 g).

From Figure 4.9, the As(III) adsorption was found to be lower than that of As(V). As(III) adsorption amount using WTR/p(APTMACl) was almost similar at all initial pH. At pH 6, the experimental results showed the higher adsorption amount of 0.04 mg/g, while for As(V) the higher adsorption amount was observed about 0.35 mg/g at pH 8. This tendency agrees with the fact that As(V) was more easily adsorbed than the As(III) in the pH range of this study.

At neutral pH, As(III) exist in solution as mainly H_3AsO_3 and $H_2AsO_3^-$ marginally [10]. At pH 6, the predominant species of As(III) is H_3AsO_3. Therefore, only smaller adsorption force was expected to occur between the positively charged on the surface of WTR/p(APTMACl) and H_3AsO_3. In the pH range of 2.2-11.5, the predominant As(V) species exist as $H_2AsO_4^-$ and $HAsO_4^{2-}$ [47]. The higher pH favors the formation of negatively charged of arsenate form, leading to higher adsorption of As(V) onto the surface of positively charged WTR/p(APTMACl). Therefore, at the pH solution between 3-10, the ionic attraction between the negative charge of arsenic species and positively charged WTR/p(APTMACl) occurred more strongly for the arsenate ions than the arsenite ions.

4.2.3 Effect of concentration of APTMACl

To obtainthe optimum APTMACl loading to WTR for the arsenic extraction, the effect of concentration of APTMACl experiments was conducted. The concentration of APTMACl was varying in the range of 250 to 2000 mM using the same former modification of WTR process. The WTR/p(APTMACl) amount was approximately 0.10 g and the initial As(V) concentration was 10 mg/L, 10 mL, pH 8 and contact time of 24 hours were studied.

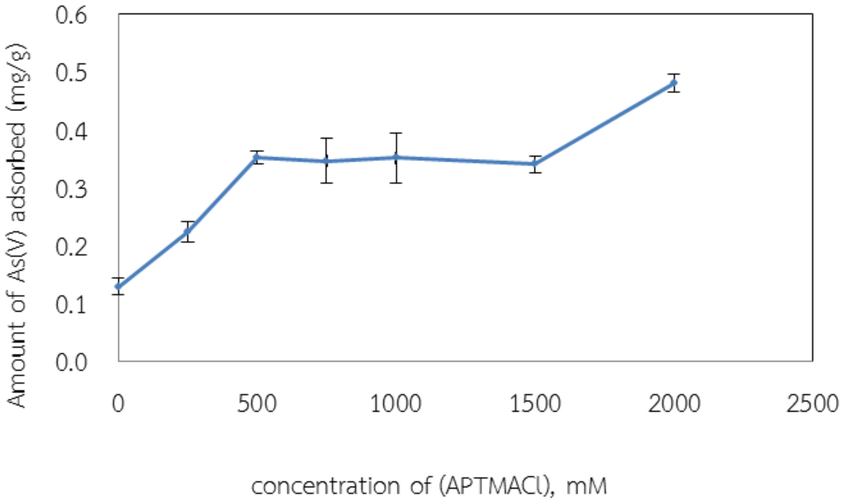


Figure 4.10 Effect of concentration of APTMACl (pH 8; drying temperature of adsorbent = 50 °C; adsorbent weight = 0.1 g).

The increase in concentration of APTMACl to WTR would be expected to increase the amount of adsorbed As(V). The results presented in Figure 4.10 indicated that as the ratio of APTMACl to WTR increased, the amount of adsorbed As(V) increased up to 0.48 mg/g. This may be due to an increase of $–N^{+}(CH_3)_3$ groups on the adsorbent. However, the higher adsorbed amount of As(V) with small amount of monomer is preferable. Thus, the concentration of APTMACl of 500 mM was selected for further experiments.

4.2.4 Effect of drying temperature of adsorbents

The effect of drying temperature of WTR/p(APTMACl) adsorbent between 50 and 100 °C on the adsorption of As(V) was investigated for initial concentration of 10 mg/L As(V) solution, pH 8, contact time of 24 hours and in various concentration of APTMACl monomer. From Figure 4.11, the adsorption amount of arsenate was higher at the lower drying temperature. This suggested that high temperature might cause the degradation of cationic polymer p(APTMACl) [36] on the surface of WTR, resulting in decreasing the efficiency of As(V) adsorption.

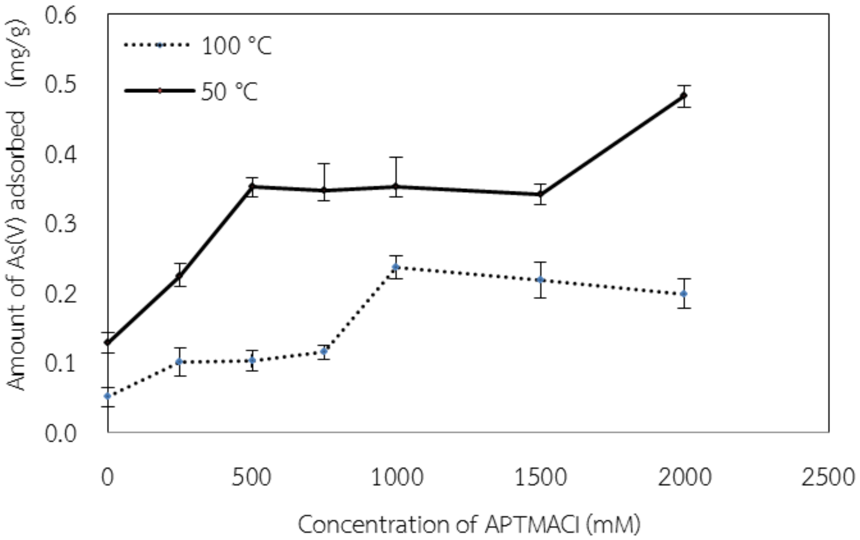


Figure 4.11 Effect of drying temperatures of WTR/p(APTMACl) at 50 and 100 °C ([As(V)] = 10 mg/L; pH 8; contact time = 24 h).

4.2.5 Adsorption isotherm

In general, adsorption isotherm is used to describe the equilibrium state of adsorbate, adsorbent and solute at a given temperature. Arsenic adsorption isotherm experiments were carried out to estimate adsorption phenomena between an ion of arsenite and arsenate in the solution and the sorbent.

The WTR/p(APTMACl) that was prepared under the optimum condition (0.5 g of WTR; 500 mM APTMACl; 50 mM TEMED; 50 mM MBA; 70 mM APS; drying temperature of adsorbent = 50 °C; 24 hrs.) was employed to extract arsenite and arsenate solution in the range of 5 to 60 mg/L. The adsorbents were allowed to adsorption arsenite from the solution at pH 6, while arsenate solution at pH 8 and for 24 hours at room temperature. The extraction of arsenite and arsenate is shown in Figure 4.12.

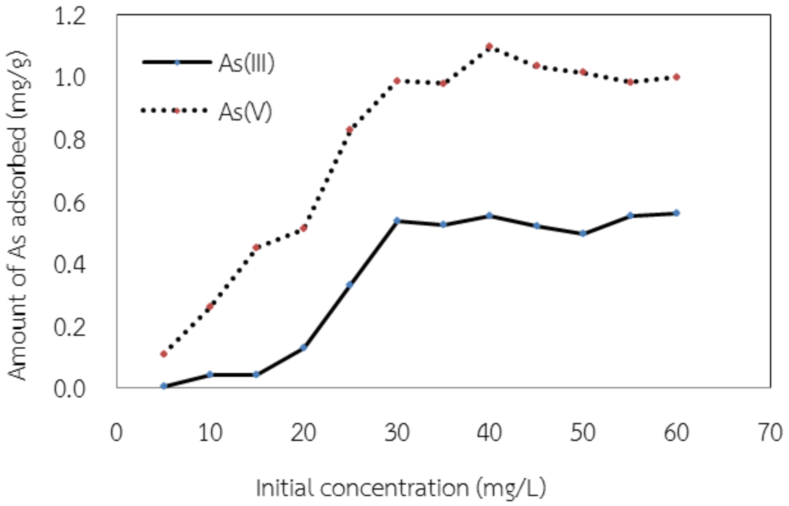
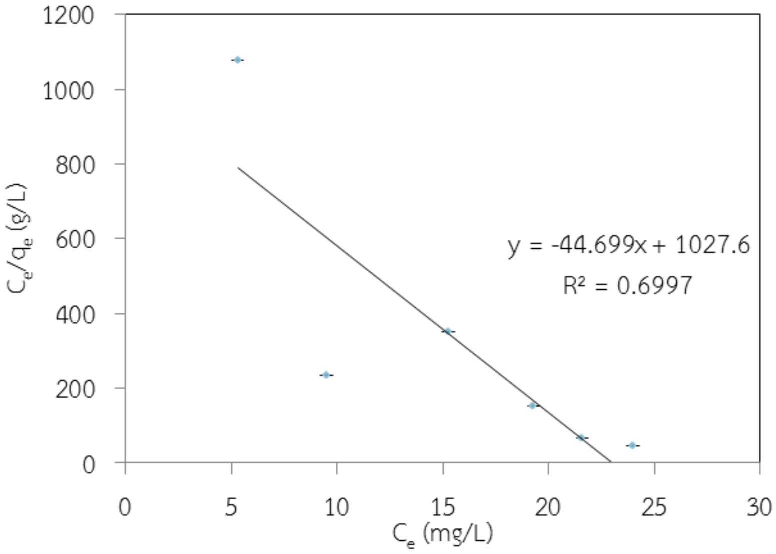
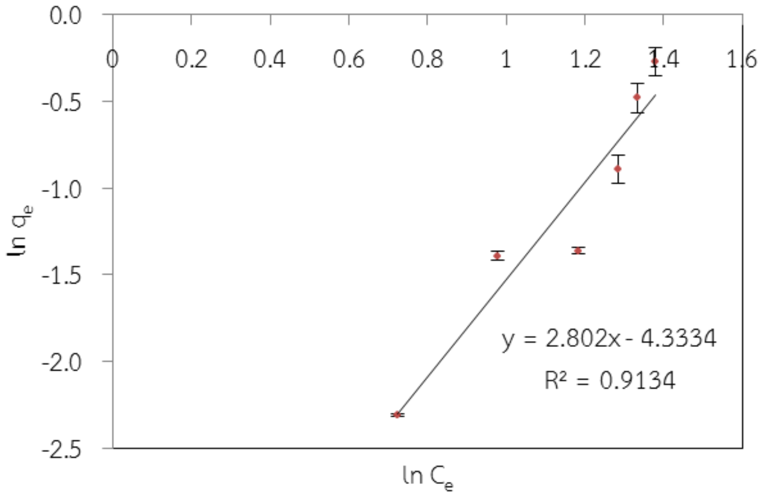


Figure 4.12 The adsorption amount of As(III) and As(V) with WTR/p(APTMACl).

Figure 4.12 displays that the amount of As(III) and As(V) adsorbed onto the adsorbent increased linearly with increasing As(III) and As(V) concentrations in the range of 5-30 mg/L and remained constant in the range of 30-60 mg/L. To study the adsorption behavior, the Langmuir and Freundlich adsorption isotherms are studied. Langmuir isotherm explains the monolayer adsorption of adsorbates on homogeneous surface with limited number of active sites and each site can adsorb only target ion via chemisorption. Freundlich isotherm model can be applied to multilayer as well as non-ideal sorption on heterogeneous surface with different adsorption energy. The linearized Langmuir and Freundlich adsorption isotherms of arsenite and arsenate were plotted in Figure 4.13 and Figure 4.14, respectively with As(III) and As(V) concentrations in the range of 5-30 mg/L.

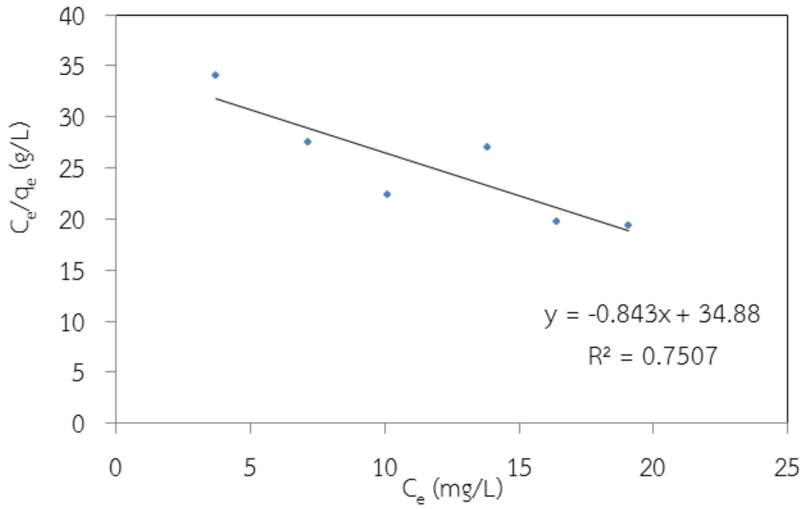


(A) Langmuir plot for arsenite adsorption

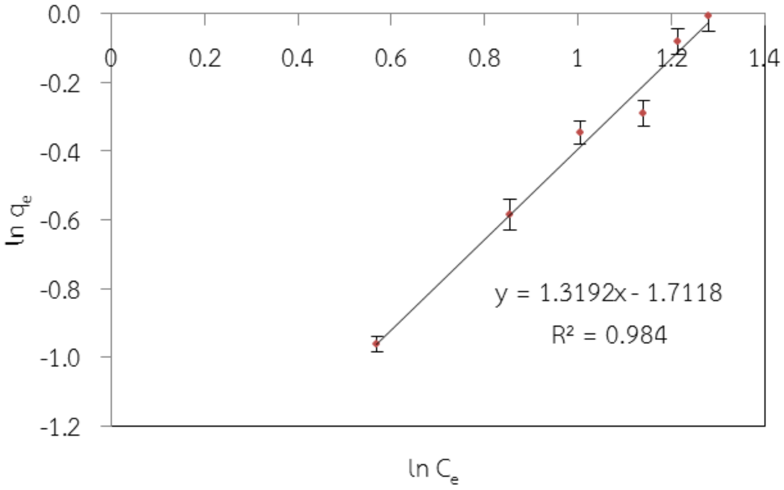


(B) Freundlich plot for arsenite adsorption

Figure 4.13 Adsorption isotherms for arsenite with concentration in the range of 5-30 mg/L.



(A) Langmuir plot for arsenate adsorption



(B) Freundlich plot for arsenate adsorption

Figure 4.14 Adsorption isotherms for arsenate with concentration in the range of 5-30 mg/L.

From the correlation coefficient (R^2) in Figures 4.13 and 4.14, the experimental data both of As(III) and As(V) adsorption fitted to Freundlich model better than Langmuir model. It reveals that As(III) and As(V) adsorption on the WTR/p(APTMACl) follows Freundlich isotherm suggesting that arsenite and arsenate ions were adsorbed as multilayer on the surface of WTR/p(APTMACl). This may reflect the irregular energy distribution on the adsorbent surface due to the presence of different groups; (i.e., amide groups and quaternary ammonium) with different activation energies [55]. The adsorption of both As(III) and As(V) was likely to occur on heterogeneous surface as mentioned in Freundlich isotherm assumption. The adsorption capacity (K_F) and adsorption intensity (n) of arsenite were calculated to be 0.0131 ($(mg/L)^{1-(1/n)}$ g^{-1}) and 0.3569, respectively, while the adsorption capacity (K_F) of arsenate was calculated to be 0.1806 ($(mg/L)^{1-(1/n)}$ g^{-1})and adsorption intensity (n) was 0.7581. The high n value of Freundlich isotherm is related to the strength of adsorption, which significantly indicates that the interaction between both As(III) and As(V) and the adsorbent is strong.

4.2.6 Effect of contact time

To attain the adsorption equilibrium time, the kinetic adsorption experiments were conducted. In former experiments, the contact time was fixed at 24 h in order to ensure the equilibrium of adsorption according to the literature [40, 42]. The amount of WTR/p(APTMACl) was controlled at 0.1 g and the initial arsenite and arsenate concentrations were 10 mg/L with solution pH 6 and 8, respectively. Profiles of As(III) and As(V) extraction by WTR/p(APTMACl) are presented in Figure 4.15.

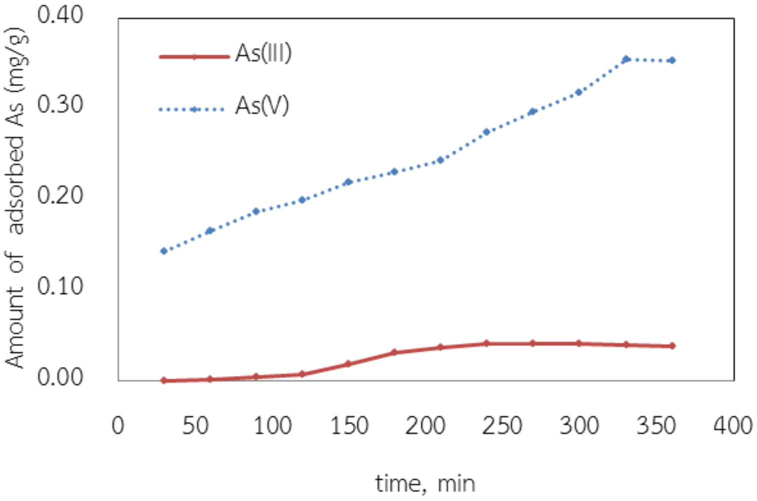


Figure 4.15 Effect of contact time on the adsorption of As(III), As(V) on WTR/p(APTMACl) ([As] = 10 mg/L;As(III) solution pH 6; As(V) solution pH 8; temperature = 25°C; adsorbent = 0.1g).

The influence of contact time for the adsorption of As(III) and As(V) on the WTR/p(APTMACl) was investigated by successively increasing the contact time from 30-360 minutes in 210 and 330 minutes, respectively. As shown in Figure 4.15, As(III) uptake rate was gradually increased within the first 210 minutes of contact time and constant state after 210 minutes. The relatively slower adsorption of As(III) can be possible that only smaller adsorption sites on adsorbent occupied by arsenite species. In addition, As(V) uptake rate was rapid within the first 330 minutes of contact time and it appeared to reach constant state after 330 minutes. This may be due to the large number of vacant spaces on the adsorbent surface and the initial strong attraction between adsorbent positive site and the negatively charge of arsenate species.

Adsorption kinetics describes the solute uptake rate, which in turn governs the residence time of adsorption reaction and is one of the important characteristics in defining the efficiency of adsorption. The pseudo-first order and pseudo-second order kinetic models were applied to model the kinetics of arsenic adsorption onto WTR/p(APTMACl), given by Equations 4.1 and 4.2, respectively.

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1}{2.303} t \tag{4.1}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{4.2}$$

where q_e and q_t are the solid-phase concentration at equilibrium and at time t, respectively.

The pseudo-first order and pseudo-second order rate constants of arsenite and arsenate determined from Figures 4.16 and 4.17 are presented in Table 4.2, along with the corresponding correlation coefficients.

Table 4.2 Pseudo-first and pseudo-second order adsorption kinetics of As(III) and As(V) onto WTR/p(APTMACl)

As	Pseudo-first order				Pseudo-second order		
	q_{exp} (mg/g)	q_e (mg/g)	K_I (min^{-1})	R^2	q_e (mg/g)	K_{II} (g/mg.min)	R^2
As(III)	0.0398	0.0706	0.0108	0.7182	0.0016	3.7361	0.8392
As(V)	0.3550	0.2940	0.0058	0.9058	0.3722	0.0316	0.9373

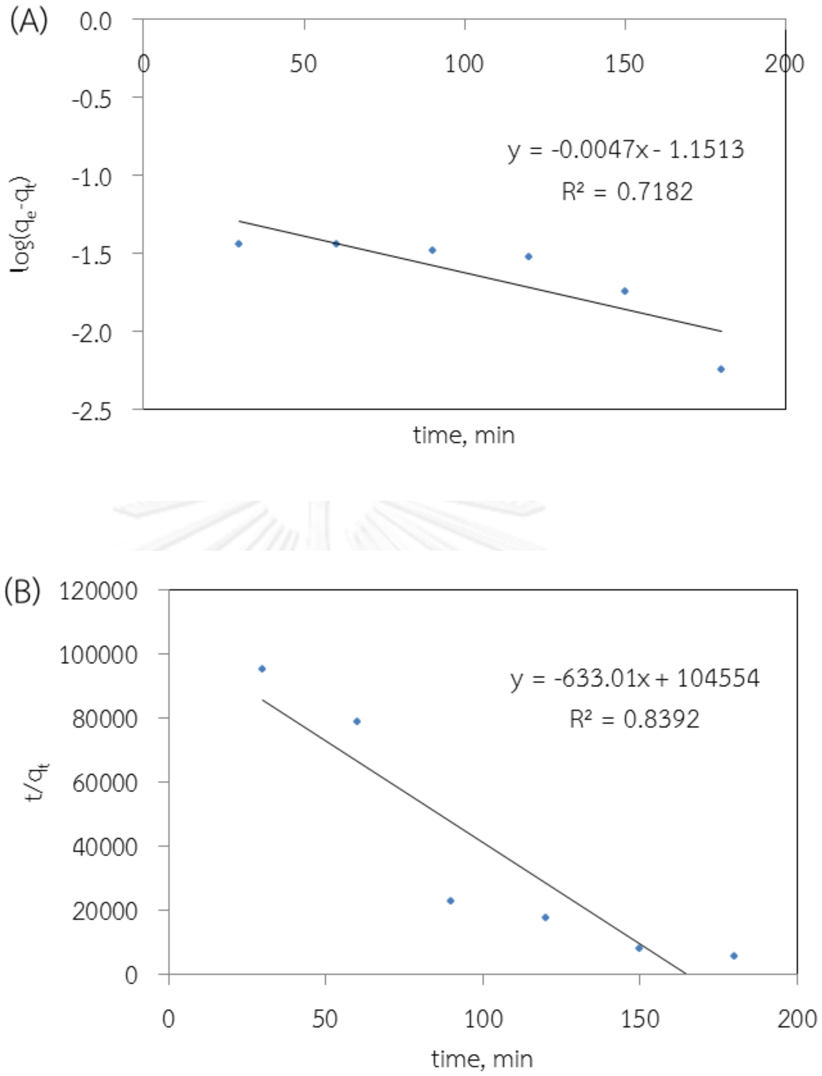


Figure 4.16 Adsorption kinetics of arsenite (A) pseudo-first order (B) pseudo-second order.

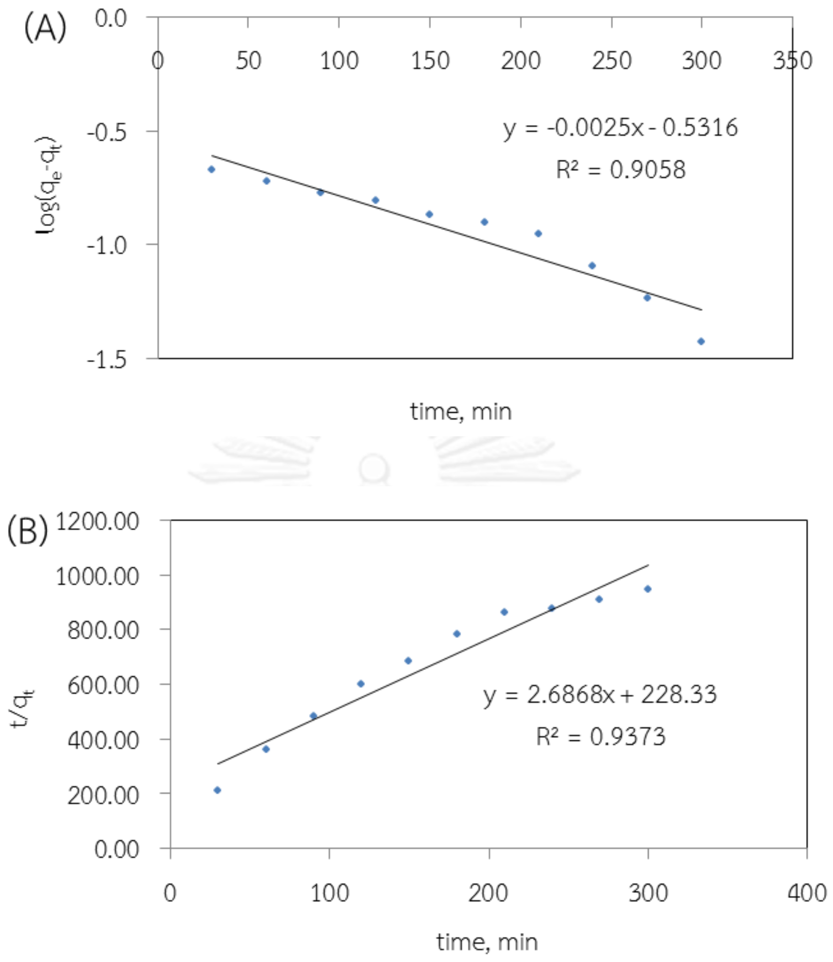


Figure 4.17 Adsorption kinetics of arsenate (A) pseudo-first order (B) pseudo-second order.

From the Table 4.2, the correlation coefficient (R^2) values of As(III) for the pseudo-second order model were higher in comparison to the values obtained for the pseudo-first order model, and the experimental adsorption capacity (q_{exp}) values of As(III) was close to the calculated adsorption capacity (q_{cal}) values for the pseudo-second order model. This suggests that the pseudo-second order model was a comparatively better-fit to describe the adsorption process of As(III) onto the

WTR/p(APTMACl) and that the pseudo-second order model, based on the assumption that the rate-limiting step may be chemical sorption or chemisorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate [39], providing the best correlation of the data. Whereas, the kinetic adsorption behavior of As(V) obeyed the pseudo-first order and the pseudo-second order model with the R^2 of more than 0.90 indicating that the rate-limiting step of As(V) may be physical and chemical sorption.

4.3 Column extraction

Based on previous observations, the WTR/p(APTMACl) adsorbent has exceptional performance in a batch extraction. However, batch type sorption is usually limited to the treatment of small volumes of effluent, whereas column extraction systems have an advantage over this limitation. In column extraction, the adsorbate is continuously in contact with a given quantity of fresh adsorbent. Hence, in the column method, various parameters influencing the arsenic adsorption were studied through the use of a home-made cylinder column.

4.3.1 Effect of flow rate

The WTR/p(APTMACl) was packed into a home-made cylinder column. The heights of columns controlled with different amounts of sorbent were 1.0, 1.5, and 2.0 cm. and they were subject to estimate its arsenic extraction efficiency under their flow rates.

Table 4.3 The arsenate extraction with various column heights of WTR/p(APTMACl) and flow rates

Column height	Weight (g)	Flow rate (mL/min)	As(V) extraction (mg/g)
1.0 cm	0.470	0.92	0.063 ± 0.023
1.5 cm	0.658	0.85	0.077 ± 0.062
2.0 cm	0.831	0.75	0.071 ± 0.059
Column height	Weight (g)	Flow rate (mL/min)	As(III) extraction (mg/g)
1.5 cm	0.667	0.85	0.014 ± 0.014

The efficiency of arsenate extraction attained from the column (in Table 4.3) were found to be increased as the column height increased with the lower the sample flow rate because of less exposure period between arsenate and the binding sites of the WTR/p(APTMACl). However, the efficiency of arsenate extraction obtained from the column height of 1.5 cm with 0.65 g of the amount of sorbent and 0.85 mL/min of the flow rate were very close to the 2.0 cm column. Therefore, to study the extraction of arsenite, the sample flow rate of 0.85 mL/min with 0.65 g the amount of sorbent was used to study and was found to be 0.014 mg/g. This result is a clear demonstration that the WTR/p(APTMACl) can adsorb arsenate higher than arsenite in the column method.

4.3.2 Desorption of adsorbents

To develop sorption process, it is essential to describe desorption of adsorbent in order to improve its cost-effectiveness by recycling adsorbent for reuse. The best desorbing agent for arsenic ions was chosen as HCl in terms of economic feasibility. To investigate for the optimal concentration of HCl was also carried out. HCl concentrations of 0.05, 0.10, and 0.50 M were tested for elution of adsorbed arsenic ions. From the Table 4.4, the desorption efficiency for arsenite and arsenate ions increased as the concentration of HCl increased. However, changes of desorption efficiency did not occur at HCl concentrations over 0.10 M HCl. Therefore, with 99% and 91% desorption efficiency of arsenite and arsenate, the 0.10 M was chosen as the optimal concentration for HCl in terms of efficiency.

Table 4.4 Effect of HCl concentration for desorption of arsenite and arsenate from WTR/p(APTAMCl); eluent volume = 25 mL, sorbent = 0.65 g, flow rate = 0.85 mL/min

Desorbing solution	Desorption, % As(III)	Desorption, %As(V)
0.05 M HCl	99.73±0.004	82.73±0.008
0.10 M HCl	99.04±0.002	91.51±0.003
0.50 M HCl	98.86±0.005	91.74±0.009

4.3.3 Breakthrough curve

A breakthrough curve was studied to determine the adsorption capacity of arsenic on a home-made cylinder column. In this experiments the adsorption efficiency of arsenite and arsenate with WTR/p(APTMACl). The home-made cylinder column was each loaded with 1.5 cm of the 0.65 g WTR/p(APTMACl) and used to adsorb arsenic from the solution passing through column at the 0.85 mL/min flow rate. The arsenic concentrations analyzed by ICP-OES.

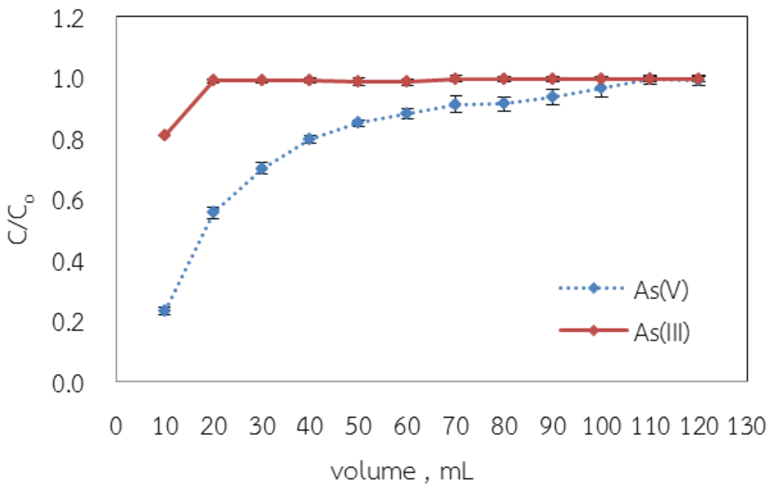


Figure 4.18 Breakthrough curves of the WTR/p(APTMACl)

The C/C_0 value versus the number of sample volumes treated by WTR/p(APTMACl) in the adsorption column is shown in Figure 4.18. It is likely that influents both of As(III) and As(V) were short-circuited through the WTR/p(APTMACl) packed column at the beginning of the column operation. Approximately 0.8 and 0.2, i.e. 80% and 20% leak, were obtained right from the As(III) and As(V) extraction process, respectively. The differences in the retention ability of As(III) and As(V) by WTR/p(APTMACl) observed here were gradually decreased and merged at the approximate volume of 110 mL. The C/C_0 value increased to 0.99, a point to which it was examined that the column completely failed to retain As(III) and As(V) at approximately 20 mL and 110 mL of the arsenic volume, respectively.

4.4 Arsenic extraction from industrial wastewater

In this experiment, the arsenic WW1 and WW2 wastewaters were exemplified. The real wastewaters were filtered to obtain the solution. These real samples were passed through the home-made cylinder column for a total of three replicates each. The arsenic extraction efficiency was calculated, and shown in Table 4.5.

Table 4.5 Arsenic extraction of wastewater

Cylinder column 0.65 g Volume 25 mL; flow rate 0.85 mL/min	Waste classification	
	WW1	WW2
Initial concentration (ppm)	112.93 ± 0.039	112.506 ± 0.033
Arsenic extraction (mg/g)	0.46 ± 0.002	0.33 ± 0.021
Arsenic extraction (%)	27%	19%

It was showed extraction efficiency (0.33-0.46 mg/g) from all real wastewaters with small volume and relatively high As concentration (>100 ppm). The lower extraction efficiency could be partially attributed to the As(III) contained in real wastewater both of WW1 and WW2 higher than As(V) as well. The arsenic extraction efficiency of WTR/p(APTMACl) (0.48 mg/g) estimated in the column study was lower than the value (0.75 mg/g) reported by Lim, J.-W., *et al.*[56]. In arsenic adsorption experiment tests with the calcination of raw sanding wastes (CSW) at Cheonju mine drainage, in Korea, the amount of arsenic adsorbed onto the CSW surface was 0.75 mg/g for an initial arsenate concentration of 1.57 mg/L. The difference in adsorption capacity might be caused by the difference in particle size and surface area as well as the active functional groups on the surface of adsorbent. Gupta *et al.*[57] studied arsenic removal with iron-chitosan composites (ICB) with arsenic obtained from Shuklagani area of Kanpur in India, they achieved high bed volumes up to reducing arsenic concentration from 500 to <10 μg/L. However, the efficiency of arsenic extraction could be achieved using WTR/p(APTMACl) by increasing the amount or height of column.

CHAPTER V
CONCLUSION AND SUGGESTION

5.1 Conclusion

The waste tyre rubber (WTR) powder in this experiment was reclaimed by microwave method at 1100 W and surface-modified by poly(3-acrylamidopropyl)trimethylammonium chloride (p(APTMACl)), polymerized by using (3-acrylaminopropyl)trimethylammonium chloride (APTMACl) as monomer, N,N”-methylene bisacrylamide (MBA) as crossliker, N,N,N’,N’-tetramethylethylenediamine (TEMED) as co-initiator, and ammonium persulfate (APS) as initiator at concentrations of 500, 50, 10, and 70 mM, respectively. Various parameters influencing the arsenic extraction were studied and optimized through batch extraction, solution pH, ratio of APTMACl to WTR, drying temperature of adsorbents, and contact time. The resulting adsorbents were characterized by particle size distribution measurement to determine the effect of reclamation by microwave method and Fourier transforms infrared spectroscopy (FT-IR). The results indicated a successful polymerization of p(APTMACl). The microwave method did not improve the arsenic adsorption efficiency of WTR. The optimal pH for the arsenite adsorption was 6 whereas the arsenate adsorption was 8. The arsenate adsorption increased gradually with increasing the monomer concentration. Comparing drying temperatures between 50 and 100 °C, the adsorption amount of arsenate was higher at the lower drying temperature. The sorption amount of arsenite and arsenate increased with increasing the initial arsenite and arsenate concentrations in the range of 5-30 mg/L. Both of As(III) and As(V) adsorption fitted to Freundlich model better than Langmuir model with the R^2 of more than 0.91 and 0.98, respectively indicating that the adsorption occurred on a heterogeneous surface. As(III) uptake rate was gradually increased within the first 210 minutes whereas As(V) uptake rate was rapid within the first 330 minutes of contact time and the rate of As(III) and As(V) adsorption could be predicted with the pseudo-second order model.

The WTR/p(APTMACl) was applied in the column extraction method. The flow rate of a home-made cylinder column was optimized at 0.85 mL/min with a sorbent weight of 0.65 g. 0.10 M HCl was a good eluent to strip As(III) and As(V) from WTR/p(APTMACl). The elution percentages of As(III) and As(V) from WTR/p(APTMACl) were 99 and 91%, respectively. The outstanding adsorption efficiency of this column for the arsenic adsorption was determined by a breakthrough curve in which the column completely failed to retain As(III) and As(V) at approximately 20 mL and 110 mL of the sample volume, respectively. To reveal the suitability of the adsorbent in optimum flow rate and volume, real arsenic containing wastewaters were studied. The WTR/p(APTMACl) was proven to be a usable adsorbent for the arsenic adsorption process and a good alternative for the waste tyre rubber management.

5.2 Suggestions for future work

- Develop and modify the waste tyre rubber from other cationic polymer such as polydiallyldimethyl-ammonium chloride (PolyDAD-MAC), polyquaternium-6, and polyacrylamide. These polymers are interesting for arsenic adsorption experiments by virtue of its high cationic charge density.

- WTR/p(APTMACl) adsorbent should be applied for other anions that can interact with a positive charge on the surface of adsorbent such as the solution of chromate (CrO_4^{2-}) and ferricyanide ($Fe(CN)_6^{3-}$).

- Automation of arsenic extraction system using WTR/p(APTMACl) should be designed and investigated.

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