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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

Adsorption of Arsenate onto Iron Oxide Coated Activated Carbon in Groundwater

Miss Manavanh Muongpak



A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Environmental Engineering
Department of Environmental Engineering
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สารหนูเป็นธาตุที่มีอยู่ทั่วไปในธรรมชาติรวมถึงน้ำใต้ดินในหลายพื้นที่ของโลกและเกิด
 จากสิ่งที่มีมนุษย์สร้างขึ้น การดูดซับเป็นหนึ่งในเทคโนโลยีที่ดีที่สุดในการกำจัดสารหนูในน้ำ
 โดยเฉพาะอย่างยิ่งสำหรับระบบผลิตน้ำดื่มที่มีกำลังการผลิตไม่มาก งานวิจัยนี้มีวัตถุประสงค์เพื่อ
 ศึกษาการดูดซับสารหนูที่มีเพนตะวาเลนต์ (As (V)) ลงบนถ่านกัมมันต์ที่ถูกเคลือบด้วยเหล็ก
 ออกไซด์ คุณสมบัติทางกายภาพและเคมีได้มีการวิเคราะห์โดยใช้กล้องจุลทรรศน์อิเล็กตรอนแบบ
 ส่องกราด (SEM) สเปกโตรสโกปีของรังสีเอกซ์ (EDX) และ การกระจายความพรุนและการ
 กระจายตัวของขนาดรูพรุน การทำทดลองแบบที่ละเท เพื่อศึกษาสภาวะที่เหมาะสมต่อการกำจัดอาร์
 ซีนต์ เช่น สภาวะพีเอชที่เหมาะสม ระยะเวลาที่เข้าสู่สมดุล ปริมาณตัวดูดซับ ตัวไอออนที่ร่วมกัน
 อยู่ในสารละลาย ผลการทดลองแสดงให้เห็นว่าประสิทธิภาพในการดูดซับสารหนูสูงสุดอยู่ที่ 90%
 ที่ค่าความเข้มข้นเริ่มต้นของสารหนู 1 มิลลิกรัมต่อลิตร ในสภาวะพีเอชที่เหมาะสม คือค่าพีเอช 5.0
 ปริมาณสารดูดซับที่ 5 กรัมต่อลิตรและระยะเวลาที่เข้าสู่สมดุล 16 ชั่วโมง ไอโซเทอมการดูดซับ
 แบบ Langmuir และ Freundlich ถูกนำมาใช้เพื่อวิเคราะห์การดูดซับสารหนูของถ่านกัมมันต์ที่
 ถูกเคลือบด้วยเหล็กออกไซด์ ซึ่งสามารถอธิบายได้ว่าโมเลกุลของสารที่ถูกดูดซับเรียงตัวเป็นชั้น
 เดียว ผลการทดลองนี้สามารถสรุปได้ว่าถ่านกัมมันต์ที่ถูกเคลือบด้วยเหล็กออกไซด์เหมาะสมที่สุดที่
 จะนำไปใช้เป็นตัวดูดซับสำหรับการกำจัดอาร์ซีนต์ออกจากน้ำที่มีการปนเปื้อน และในการทดลอง
 แบบกรองต่อเนื่องในคอลัมน์ที่บรรจุถ่านกัมมันต์ที่ถูกเคลือบด้วยเหล็กออกไซด์ ด้วยการป้อนน้ำที่
 ปนเปื้อนสารหนูแบบไหลขึ้นที่อัตรา 1 มิลลิตรต่อนาที ผลการทดลองพบว่า ระยะเวลาที่เข้าสู่การ
 อิ่มตัว (หรือสถานะที่น้ำที่ผ่านชั้นกรองมีความเข้มข้นเท่ากับน้ำเข้าระบบ) อยู่ที่ 120 ชั่วโมง และ
 Thomas Model ให้ผลลัพธ์ที่ดีที่สุดในการอธิบายเส้นโค้งของการพัฒนาการอิ่มตัว ถ่านกัมมันต์ที่
 ถูกเคลือบด้วยเหล็กออกไซด์ได้ถูกนำกลับมาใช้ใหม่ โดยทำการฟื้นฟูโดยใช้ NaOH เข้มข้น 0.1M
 ซึ่งสังเกตได้จากผลของการใช้ตัวดูดซับที่ผ่านการฟื้นฟู เห็นได้ว่ามีประสิทธิภาพเทียบเท่ากับวัสดุ
 ดูดซับใหม่

ภาควิชา วิศวกรรมสิ่งแวดล้อม

ลายมือชื่อนิสิต

สาขาวิชา วิศวกรรมสิ่งแวดล้อม

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Arsenic is an abundant element that exists in both natural and anthropogenic sources, including groundwater in many parts of the world. Adsorption is one of the best technologies for arsenic removal from water, particularly for a small-scale system. The aim of this study was to investigate the arsenate (As(V)) adsorption onto iron oxide coated activated carbon. The physicochemical properties were characterized by scanning electron microcopy (SEM) with energy dispersive X-ray spectroscopy (EDX), porosity and pore size distribution analysis. Batch experiment was conducted to examine the effects of the equilibrium solution pH, adsorbent dosage, contact time and co-existing ions on arsenate removal. The results indicate that the maximum arsenate adsorption efficiency is achieved 90% in the condition of equilibrium pH 5.0, adsorbent dosage of 5 g/L and contact time of 16 h with the initial arsenate (As(V)) concentration of 1 mg/L. Langmuir and Freundlich models were used to determine the adsorbent capacity for arsenate removal by iron oxide coated activated carbon. The Rapid Lab-Scale Column study was carried out by using iron oxide coated granular activated carbon (Fe-GAC) as an adsorbent for the removal of arsenate (As(V)) with flow rate 1 mL/min. The results showed that the breakthrough time was reached at 120 hours. The breakthrough curves showed that the Thomas model gave the best result for the operating condition. Iron oxide coated activated carbon was regenerated by using 0.1M NaOH, it is observed by effect of regeneration cycles that the regenerated adsorbent was almost as efficient as the new adsorbent.

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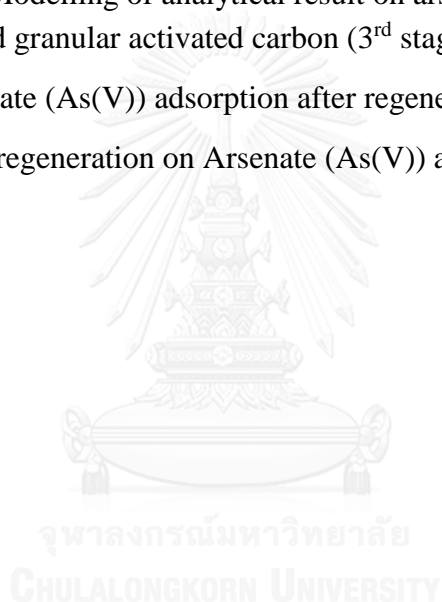
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CHAPTER 1

INTRODUCTION

1.1 Background

Arsenic is a ubiquitous element that has found in rock and soil, air, water and some plant and animal. Arsenic exists in oxidation states of -3, 0, 3 and 5. It is released into the environment through nature and human activities (*Tuna et al., 2013*). Natural sources consist of the washout and erosion of arsenic from minerals, ores, and soil, which possibly occurs because of long-term exposure against geochemical changes. Anthropogenic sources consist of forestry, agriculture application of pesticides, herbicides and fertilizers, and industrial effluents from metallurgy, electronics, mining, glass processing, ceramic, pharmaceuticals, dye and pesticide, wood preservative, petroleum refining and landfill leaching (*Budinova et al., 2009; Kim et al., 2002; Smedley and Kinniburgh, 2002*). In oxygenated water, it is mostly present as arsenate (e.g. AsO_3^- , AsO_4^{3-}), which has an oxidation state of 5. Under reducing conditions (e.g. deep lake sediments, groundwater), it is present as arsenite (e.g. AsO_2^-), which has an oxidation state of 3.

Arsenic contamination of 1.0 mg/L has been found in groundwater in the southern part of Laos (Champasak province), which exceeds to WHO's guideline of 10 $\mu\text{g/L}$. Arsenic contaminated water harms many people in that area. Arsenic poisoning, an especially inorganic form has extremely affected human health; it is a serious problem worldwide. Consumption of arsenic contaminated water even in a low concentration can cause diseases in lung cancer, kidney, bladder, liver, skin, cardiovascular diseases, and chronic bronchitis (*Asadullah et al., 2014; Hughes, 2002; Jain and Ali, 2000; Kapaj et al., 2006*).

There are many technologies commonly used to eliminate arsenic in liquid phase including alum coagulation/precipitation, oxidation/precipitation, granular ferric hydroxide, reverse osmosis and nano-filtration, ion exchange and coagulation-microfiltration (*Kartinen and Martin, 1995; Viraraghavan et al., 1999; Zouboulis et*

al., 1993). However, these technologies are expensive and difficult to apply in the rural areas. Furthermore, these technologies produce a huge volume of sludge, which needs further treatment before final disposal. Adsorption is one of the best available technologies for arsenic removal in water treatment because it is not complicated, it produces less sludge and it is a low-cost and high-efficiency technology for eliminating a small amount of heavy metal from water (*Jang et al.*, 2006).

From the reasons mentioned above, the adsorption process is selected due to it is very convenient and low-cost for the operation, which is suitable for a small community in developing country. Four types of adsorbent were used in this research including powdered activated carbon, granular activated carbon, iron oxide coated powdered activated carbon and iron oxide coated granular activated carbon. Impregnation of iron oxide to activated carbon has been reported to improve adsorption capacities and mechanical properties of the activated carbon (*Chen et al.*, 2007; *Fierro et al.*, 2009; *Jang et al.*, 2008). Moreover, this research also studied the optimum conditions and evaluated the adsorption efficiency in eliminating arsenate in synthetic water, which made from sodium arsenate dibasic heptahydrate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$) for applying in eliminate arsenic in a small community and having safe water for consumption.

1.2 Research objectives

- To characterize the surface structure of the adsorbents, in terms of specific surface area and pore size distribution of virgin and iron oxide coated activated carbons.
- To study the influencing factors, i.e. solution pH, contact time, adsorbent dosage, ionic strength, and co-existing ions, on the arsenate adsorption onto virgin and iron oxide coating activated carbons.
- To compare the arsenate adsorption efficiency and evaluate the treatment cost among four adsorbents tested.

1.3 Research Hypotheses

- The repeatedly coating of iron oxide on activated carbons can increase the amount of iron oxide coated on activated carbons due to multi-layer coating.
- Iron oxide coating on the activated carbon can enhance the arsenate adsorption capacity from arsenic-containing synthetic groundwater.
- Solution pH, contact time, adsorbent dosage, ionic strength, and coexisting ions might affect the arsenate adsorption efficiency because pH, ionic strength and co-existing ions induce competitive effects on the arsenic adsorption while increasing adsorbent dosage provides more adsorptive sites for arsenic.

1.4 Scope of research

All experiments were conducted in the laboratory of department of environmental engineering under the room temperature ($25^{\circ}\text{C} \pm 2$). The scope of the research is as follows:

- Arsenic-contaminated water samples were collected from different wells in southern part of Laos and were analyzed by using ICP-OES in accordance with the US EPA Method 200.5.
- The adsorbent used in this research is FILTRASORB 200 granular activated carbon, which is made from a selected grade of bituminous coal, it was grounded by cup mill to generate virgin powdered activated carbon.
- Coating of activated carbon was carried out by an impregnation method using the 0.5 M Ferrous chloride solution following the method reported elsewhere (*Chang et al., 2010*).
- After coating activated carbon with iron oxide, the adsorbents were measured by SEM-EDX and Pore Distribution Analyzers.
- The experiment was conducted by using a batch adsorption test with varied solution pH, contact time, adsorbent dosage, ionic strength and coexisting ions.

- After the experiments, the analysis of arsenic in water samples was conducted via a Spectro Genesis Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) in accordance with US EPA Method 6020.
- Comparison the adsorbents based on the arsenate adsorption efficiency was done to choose the most effective adsorbent for arsenate removal to make the column experiment.
- The column experiment was carried out by using an acrylic pipe, the size of a column was calculated by the optimum value obtained from the batch adsorption experiment.
- Regeneration of iron oxide coated granular activated carbon was performed to evaluate the cost of treatment among the difference adsorbent.

1.5 Thesis structure

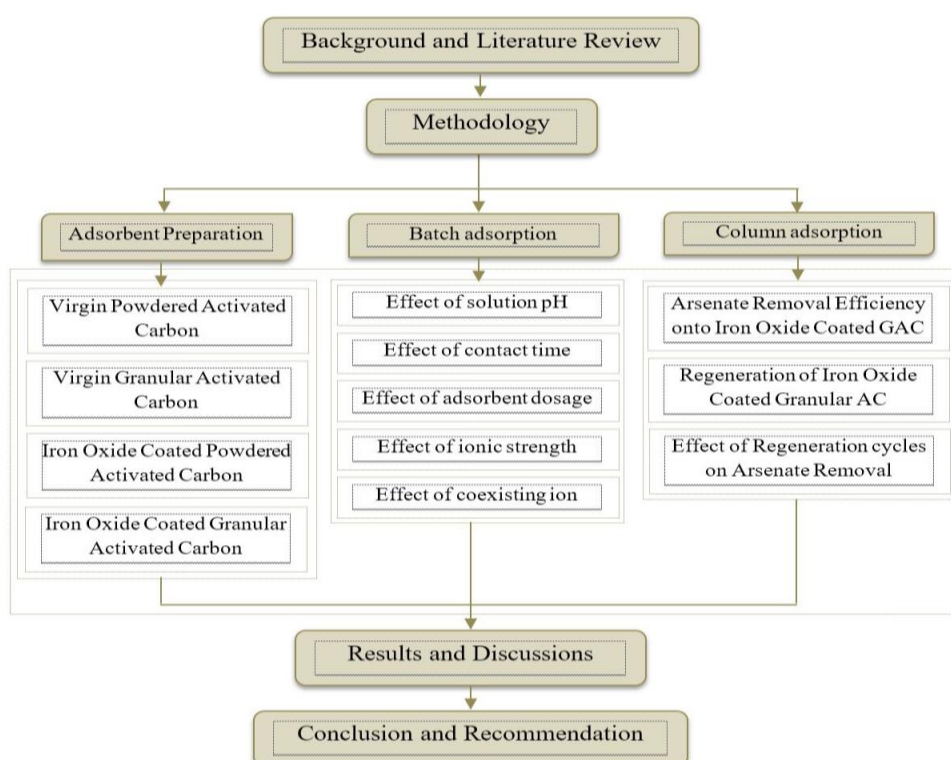


Figure 1.1 Overview of this research

CHAPTER 2

BACKGROUND AND LITERATURE REVIEW

2.1 Arsenic

2.1.1 Arsenic properties

Arsenic (As) is a ubiquitous element, which demonstrates characteristics of a metalloid. It occurs naturally in the earth's crust mainly in minerals and ores and anthropogenic source (*Selene et al., 2003; Smedley and Kinniburgh, 2002; Wang and Mulligan, 2006*). It is widely dispersed throughout the environment in the land, water and air. Arsenic appears in the environment in various oxidation states such as -3 (arsine gas, AsH_3), 0 (zero-valent), +3 (the arsenite) and +5 (the arsenates) but it is mostly found in natural water as AsO_3^{3-} arsenite and AsO_4^{3-} arsenate. As(III), typically found in anaerobic groundwater, is more toxic than As(V), while As(V) is found in an oxidized condition (*Mohan and Pittman, 2007; Sullivan et al., 2010*).

Trivalent arsenic (+3) or arsenite species are $\text{As}(\text{OH})_3$, $\text{As}(\text{OH})_4^-$, $\text{AsO}_2\text{OH}^{2-}$ and AsO_3^{3-} while pentavalent (+5) or arsenate species include AsO_4^{3-} , HAsO_4^{2-} , H_2AsO_4^- . Redox potential (Eh) and pH are the most significant factors controlling arsenic speciation. At high redox potential (Eh), arsenic is stabilized as series of pentavalent arsenic species (H_3AsO_4 , H_2AsO_4^- , HAsO_4^{2-} , AsO_4^{3-}) whereas under most reduced (acid and mildly alkaline) condition and low redox potential, the trivalent arsenic species (H_2AsO_3 , H_2AsO_3^- , HAsO_3^{2-} , AsO_3^{3-}) become stable.

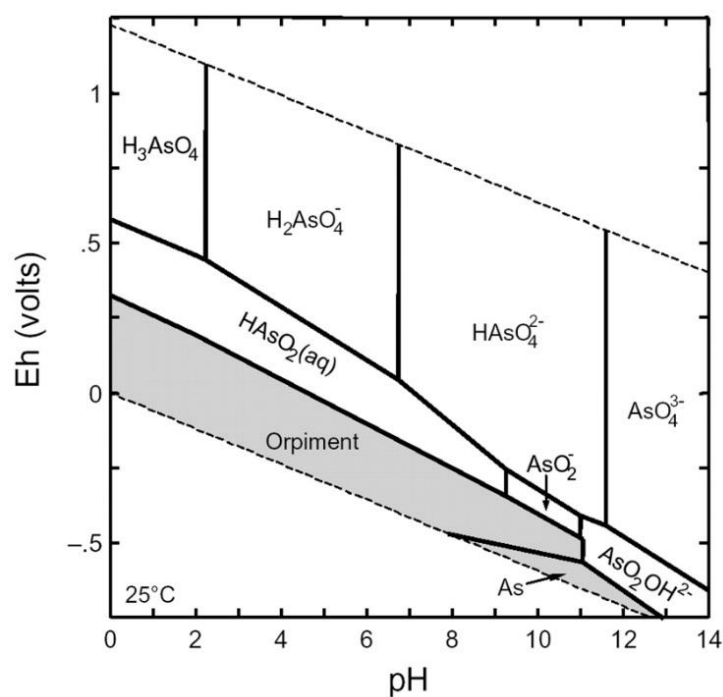


Figure 2.1 Diagram of redox potential (Eh) and pH for As at 25 °C and 1 atm
(Smedley and Kinniburgh, 2002)

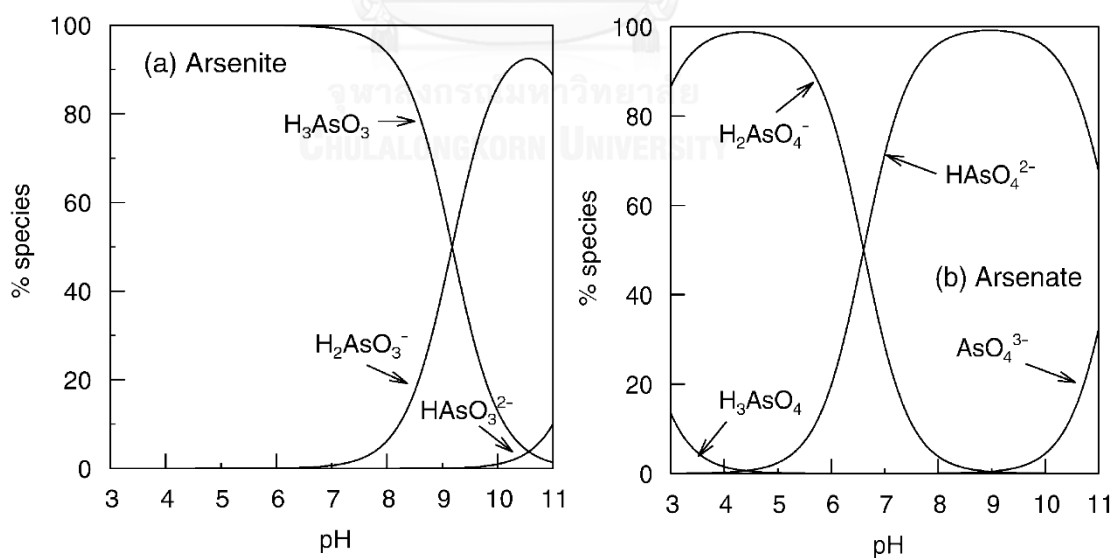


Figure 2.2 Arsenite species in function of pH and arsenate species in function of pH
(Smedley and Kinniburgh, 2002)

2.1.2 Arsenic poisoning

Inorganic species of arsenic (As(III) and As(V)) are present in water, soil, air and food. Water and soil are the main media of human exposure to arsenic by contact with skin, inhalation, and consumption because arsenic accumulates in plants, vegetable and other fruits that grow in contaminated soil and it is a pathway of arsenic to exposure in the food chain (*Meharg and Hartley-Whitaker, 2002*). The toxicity of arsenic depends on the chemical forms and oxidation states. High toxicity of arsenic in groundwater is a serious problem worldwide, which affects millions of people (*Smedley and Kinniburgh, 2002*). The World Health Organization (WHO) recommends a maximum level of arsenic in drinking water of 10 µg/L (*WHO, 2011*). Nevertheless, approximately 50 million people worldwide still face with high arsenic concentration in drinking water, soil and air (*Smedley and Kinniburgh, 2002*). Arsenic causes acute and chronic adverse health effects in lung cancer, kidney, liver, skin, urinary bladder, cardiovascular disease, and chronic bronchitis (*Asadullah et al., 2014; Hughes, 2002; Jain and Ali, 2000; Kapaj et al., 2006*).

2.2 Arsenic treatment technology

Rural area of many countries is facing with arsenic contamination in groundwater, which has high arsenic concentration more than standard. Thus, numerous procedures are available for eliminating arsenic from water including conventional coagulation, sorption with ferric and aluminum oxides, ion exchange, and membrane filtration (*Crittenden et al., 2012*).

2.2.1 Coagulation process

Coagulation is a traditional process that uses alum, ferric chloride, ferric sulfate, or lime as coagulants for removing arsenic. Arsenic in form of arsenate (As(V)) can be removed by coagulation followed by filtration process; if arsenic is present in the form of arsenite (As(III)), chlorine, permanganate or ozone are used for oxidizing As(III) to As(V).

Previous study showed that coagulation with ferric chloride (FeCl_3) is more effective than other coagulants for arsenic removal from drinking water (*Wung et al., 2014*). For simultaneous treatment of arsenic and phosphate or silica, coagulation becomes less effective for arsenic removal (*Crittenden et al., 2012*).

2.2.2 Adsorption process

Adsorption is one of the most frequently used technologies to eliminate heavy metals due to its high efficiency, low-cost and no sludge produced. Iron oxide coated activated carbon is the most widely used adsorbent for arsenic removal due to its higher removal capacity by comparing with traditional adsorbents, it has high surface area, which result in high removal efficiency (*Mohan and Pittman, 2007*).

Several studies have investigated on the removal of arsenic by using iron oxide modified, over than 80% of arsenic removal efficiency are achieved (*Tuna et al., 2013*).

2.2.3 Ion exchange process

Ion exchange is one of the best technologies for removing arsenic from drinking water, considered by US EPA (*EPA, 2000*). However, ion exchange process produces a bulky volume of arsenic-laden regenerate brine, which is often classified as hazardous process waste residual and needs expensive additional treatment, handling, and disposal (*Byungryl et al., 2011*).

2.2.4 Membrane process

Membrane processes, particularly reverse osmosis, have been confirmed as the best technology for the arsenic removal. It can completely treat water and meet the water regulations. Both laboratory and pilot-scale experiments have been shown that above 95% of As(V) and 74% of As(III) removal efficiencies can be achieved by the Reverse Osmosis process (*Höll, 2010; Katsoyiannis and Zouboulis, 2006*). Membrane processes dispose of arsenic through size exclusion, electric repulsion, and adsorption of As containing compounds (*Sachin et al., 2015*).

2.2.5 Reverse Osmosis

Reverse osmosis (RO) is one of the technology for water purification, by using a semipermeable membrane to eliminate dissolved contaminant out of water. It can eradicate ions and molecules from liquid phase including bacteria, which is commonly used in both industrial production and the drinking water processes. In reverse osmosis, the pure solvent can pass to the other side of membrane, while the solute is retained on the membrane. The large molecules or ions are not allowed to pass through the pores, but it allows the smaller components (i.e. solvent) pass through freely.

2.3 Adsorption process

2.3.1 Adsorption mechanism

Adsorption is the process by which molecules of substance collect on the surface of another solids or liquids. The substances that attract molecules or ions to sorb on the surface called adsorbent such as activated carbon, clay minerals while the molecules or ions that adhere is called adsorbate which is found at contact surface between solids – gas, liquids – gas, liquids – solids, liquids – liquids and solids – solids.

Adsorption process is a practical process that has high efficiency in treatment and durable with high toxic chemical. In water treatment process, adsorption has been demonstrated as an efficient removal process for a diversity of solutes (*Worch, 2012*). Otherwise, adsorption is a low-cost process and requires small space for operation and low maintenance cost.

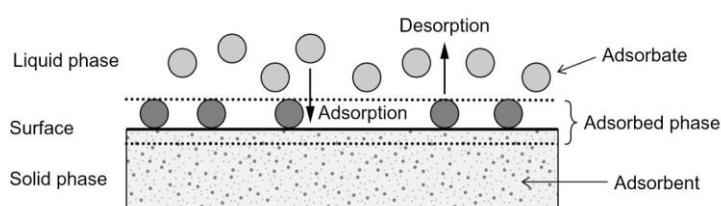


Figure 2.3 Adsorption Mechanism

2.3.2 Influencing factors in adsorption process

2.3.2.1 Adsorbent properties

Size and specific surface area are directly related to the ability of adsorption. However, in some cases a high specific surface area may not lead to high adsorption capacity due to the effect of surface chemistry of adsorbent including molecular weight, polarity, solubility, and chain length, on adsorption. The adsorption rate is inversely proportional to the adsorbent size: i.e. power activated carbon, which has a smaller size, has a higher adsorption rate than granular activated carbon on the same adsorbent mass basis.

2.3.2.2 Adsorbate properties

Adsorption efficiency is inversely related to the adsorbate solubility. Adsorption will be increased, if the adsorbate solubility decreased. Non-polar adsorbate tends to produce more adsorption capacity than polar adsorbate due to the ease of transfer for non-polar adsorbate in water. Furthermore, molecular weight, chain length, polarity and degree of ionization are also important factors to be considered.

2.3.2.3 Potential of hydrogen (pH)

The pH value is a primary dominance in adsorption efficiency for ionized and water solubility of substances. Furthermore, hydrogen ion has high solution in the adhered surface area of adsorbent.

2.3.2.4 Temperature

Temperature has influence to adsorption rate and adsorption efficiency since the adsorption rate increases by increasing temperature. But the adsorption efficiency will decrease at high temperature and increase at low temperature because of the adsorption is exothermic reaction.

2.3.2.5 Contact time

Contact time is one of the parameter that affects the adsorption efficiency and lifetime of the adsorption in column. Contact time is associated with the adsorption efficiency only for a period of time. If the adsorption reached the equilibrium point, contact time will not affect the adsorption efficiency.

2.3.3 Adsorption isotherm

Adsorption isotherm refers to characterization of adsorption process and the amount of adsorbate on the adsorbent. There are 5 basic types of adsorption isotherms as shown in *Figure 2.4* in which type I is monolayer adsorption and type II-V are multilayer.

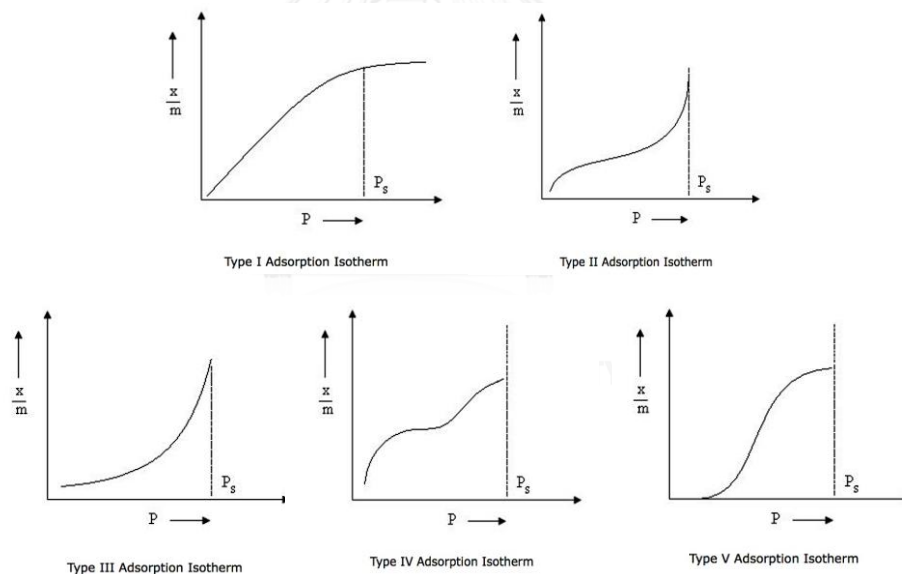


Figure 2.4 Basic type of adsorption isotherm (Faust and Aly, 2013)

2.3.3.1 Freundlich adsorption isotherm

Freundlich adsorption isotherm was widespread explained in adsorption process in liquid. Equation follows:

$$\frac{X}{m} = KC_e^{1/n} \quad \text{Eq. 2.1}$$

where:

X/m mass of adsorbed adsorbate per adsorbent weight (mg/g)

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

K and n constant value depend upon adsorbent and gas

Its linearized form can be written as follow:

$$\log (X/m) = \log K + (1/n) \log C_e \quad \text{Eq. 2.2}$$

The plot between $\log C_e$ and $\log (x/m)$, $1/n$ is a value of slope and $\log k$ is y-axis intercept.

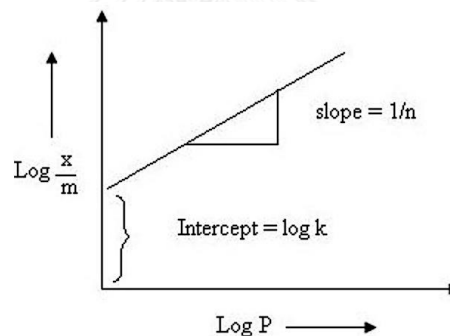


Figure 2.5 Freundlich adsorption isotherms (Sundstrom and Klei, 1979)

2.3.3.2 Langmuir adsorption isotherm

Langmuir adsorption isotherm or localized monolayer model, the molecule is attracted to the surface of adsorbent. In each molecule, the adsorption is a single molecule by adsorption area has a certain value, which defined by the characteristic of surface and adsorption energy and each area has the same value. The equation for Langmuir adsorption isotherm follows:

$$X = \frac{X_m b C_e}{1 + b C_e} \quad \text{Eq. 2.3}$$

where:

$X = X/m$ mass of adsorbed adsorbate per adsorbent weight (mg/g)

C_e equilibrium concentration of adsorbate in solution (mg/g)

X_m the amount of substance

B constant value of adsorption energy

It also can be written as a linearized form:

$$\frac{1}{X} = \frac{1}{bX_m C_e} + \frac{1}{X_m} \quad \text{Eq. 2.4}$$

The plot a graph between $1/X$ and $\log 1/C_e$, we will get a straight line and find the constant value of X_m and b by slope and y-axis intercept.

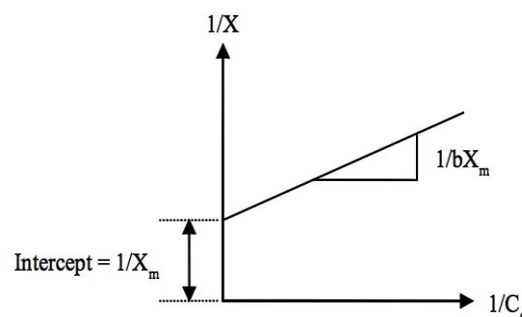


Figure 2.6 Langmuir adsorption isotherms (Sundstrom and Klei, 1979)

2.3.4 Column adsorption

Although, the batch adsorption experiments provide the important data on characteristics of adsorption equilibrium and adsorption kinetic. Nevertheless, the data acquired are not adequate to give exact scale-up data needed in designing the column for adsorption. Hence, the column adsorption experiment is required to determine the breakthrough point which is used to determine the lifespan of fixed bed adsorbent (Bielicka-Daszkiwicz and Voelkel, 2009; Chu, 2004; Naja and Volesky, 2006; Saad et al., 2015).

2.3.5 Modelling of analytical results for column adsorption

For designing the effective column adsorption with the optimum condition, Adams-Bohart, Yoon-Nelson and Thomas models are important to predict the dynamic behavior of the columns.

2.3.5.1 Adams-Bohart model

Adams-Bohart model was established to explain the relationship between (C_t/C_0) and time. The model describes the first step of the breakthrough curve and emphasizes on some parameters i.e. the maximum adsorption capacity (N_0) and kinetic constant K_{AB} (Aksu and Gönen, 2004; Chowdhury et al., 2012). The Adams-Bohart model equation is expressed as:

$$\ln(C_t/C_0) = K_{AB}C_0t - K_{AB}N_0(Z/U_0) \quad \text{E.q 2.5}$$

where C_0 and C_t are the initial and final adsorbate concentrations, respectively (mg/L), Z is the fixed-bed height (cm), U_0 is the flowrate (cm/min), N_0 is the saturation concentration (mg/L), and K_{AB} is the kinetic constant (L/mg.min). K_{AB} and N_0 can be calculated from the intercept and slope of the plot of $\ln(C_t/C_0)$ against time (t).

2.3.5.2 Yoon-Nelson model

Yoon-Nelson model is a simple model that not required data about the adsorbent type or the physical characteristic of the column. It was described the adsorption breakthrough curve. The model was derived on the assumption that the possibility of adsorbate breakthrough on the adsorbent is proportional to the rate of decrease in the probability of adsorption for each adsorbate molecule (Aksu and Gönen, 2004; Chowdhury et al., 2012). The linearized model for a single component system can be written as:

$$\ln\left(\frac{C_t}{C_0 - C_t}\right) = K_{YN}t - TK_{YN} \quad \text{E.q 2.6}$$

where K_{YN} is the rate constant (min^{-1}), T is the time required for 50% adsorbate breakthrough (min) and t is the time of breakthrough (min). K_{YN} and T can be calculated from the plot of $\ln(C_i/C_0 - C_i)$ vs. t . If the theoretical model precisely characterizes the experimental data, this plot will be result in a straight line with a slope of K_{YN} and intercept of TK_{YN} .

2.3.5.3 Thomas model

Thomas model is the most widely used model to describe column performance which based on the assumption of the adsorption behavior follows Langmuir isotherm and assumes the rate driving forces obeys the second-order reversible reaction kinetics (*Thomas, 1944*). The Thomas model equation is given as:

$$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{K_{Th}C_0q_0m}{Q} - \frac{K_{Th}C_0}{Q}(V_{eff}) \quad \text{E.q 2.7}$$

where K_{Th} is the rate constant ($\text{mL}/\text{mg}\cdot\text{min}$), q_0 is the equilibrium adsorbate uptake (mg/g), m is the adsorbent amount in the fixed-bed column (g), V_{eff} is the effluent volume (mL), and Q is the flowrate (mL/min). K_{Th} and q_0 can be calculated from the slope and intercept of the linear plotting between $\ln(C_i/C_0-1)$ vs. V_{eff} .

2.4 Activated carbon and iron oxide coated activated carbon

Activated carbons are made from carbonaceous materials by the oxidation of the carbon atoms found on the inner and outer surfaces (*Mattson and Mark, 1971*). These materials had the large specific surface areas, well-developed porosity and tunable surface-containing functional groups (*Baker et al. 1992, Zongxuan et al., 2003*). Therefore, activated carbons are widely used as an effective adsorbent for removing the organic chemicals and metal ions from gases, air, water and wastewater (*El- Hendawy 2003*).

2.4.1 Activated carbon category

Activated carbon can be categorized by particle size, which can be divided into 4 main types:

2.4.1.1 Powdered activated carbon (PAC)

Powdered activated carbon is a fine carbon material, which is made up by crushed carbon particles form as fine granules or powder. It is commonly used to add directly to the rapid mix basin, raw water intakes or gravity filters. The ASTM categorizes particles passing through an 80-mesh sieve with the average diameter of 0.177 mm.

2.4.1.2 Granular activated carbon (GAC)

Granular activated carbon has a larger particle size compared to powdered activated carbon which is widely applied for vapor absorption and water purification due to the rapid diffusion of vapors and gases. The 8×30 and 12×40 mesh sieve of GAC were designed for applying in liquid purification due to the size balance, surface area and head loss characteristics.

2.4.1.3 Extruded activated carbon (EAC)

Extruded activated carbon is made from the mixing of powdered activated carbon with a binder and extruded into a cylindrical with the average diameters from 0.8 to 130 mm shaped activated carbon block. Due to the low pressure drop and high mechanical strength, the extruded activated carbon was mostly used for vapor absorption.

2.4.1.4 Bead activated carbon (BAC)

Bead activated carbon is made from petroleum pitch and supplied in diameters from approximately 0.35 to 0.80 mm. Similar to EAC, it is also noted for its low pressure drop, high mechanical strength and low dust content, but with a smaller grain

size. Its spherical shape makes it preferred for fluidized bed applications such as water filtration.

2.4.2 Advantage of activated carbon

- Activated carbon or charcoal products effectively remove pollutants, contaminants and other impurities from water, air, food and beverages, pharmaceuticals and more.
- Natural filter media: this water filter media is created from materials such as bituminous, wood and coconut shell, no chemicals or other substances are added to water, therefore a natural filtration process is achieved.
- Low-cost & easy maintenance: AC filters are one of the least expensive filters and don't require much in terms of maintenance. Each brand and model of AC filter cartridge has a certain service life at the end of which the filter cartridge has to be replaced;
 - Excellent for enhancing the taste and odor of tap water;
 - Good at filtering out other carbon-based, organic chemicals and chemical disinfectants like chlorine as well as some microorganisms.

2.4.3 Activated carbon property in adsorption

Activated carbon is a form of carbon that has been processed to create millions of tiny pores between the carbon atoms, resulting in a dramatically increased surface area. The surface area of activated carbon makes the materials suitable for adsorption, a process by which impurities are removed from fluids, vapor or gas.

2.4.4 Iron oxides coated activated carbon property in adsorption

Iron oxides are chemical compounds composed of iron and oxygen. Altogether, there are sixteen known iron oxides and oxyhydroxides. Iron oxides and oxide-hydroxides are widespread in nature, play a significant role in several biological, chemical and geological processes and iron oxides are commonly used as low-cost, colored concretes, durable pigments in paints, and coatings.

Iron oxides are well known as a strong affinity to arsenic in water as a result of their partial positive charge and large surface areas (*Lin and Wu, 2001*). Iron oxides are used to coat or impregnate on solid materials to increase the adsorption ability of the solid materials. Iron oxide coated activated carbon was found as an effective adsorbent in removing As(V) from an aqueous solution. *P Mondal et al. (2008)* found that using 8 g/L of Fe-GACs with 4.78% of iron content can reduce arsenic concentration below 10 ppb and 50 ppb from arsenic solutions containing initial arsenic value of 200 ppb and 520 ppb, respectively. At acidic condition, Fe-GACs performed well on arsenate adsorption. Especially, the arsenate removal efficiency was maintained close to 100% with pH lower than 6 and declined quickly with pH above 7, because the surface charge of Fe-GAC and arsenic species in liquid phase depend on solution pH. (*Chang et al., 2010*).

2.5 Regeneration of adsorbents

Regeneration/desorption is one of the important part as it controls the budget of water treatment technology in heavy metal removal processes (*Ali, 2012*). For the effective regeneration of adsorbents and metal recovery, acids (such as HCl, H₂SO₄, HNO₃, HCOOH and CH₃COOH), alkalis (such as NaOH, NaHCO₃, Na₂CO₃, KOH and K₂CO₃), salts (such as NaCl, KCl, (NH₄)₂SO₄, CaCl₂.2H₂O, NH₄NO₃, KNO₃ and C₆H₅Na₃O₇.2H₂O), chelating agents and deionized water (DI), buffer solutions (such as bicarbonate, phosphate and tris) were used in several researches. Several alkalis were similarly used for the regeneration of heavy metals, i.e. NaOH, NaHCO₃, Na₂CO₃, KOH and K₂CO₃. The recovery of heavy metal was found to be 94.6–98.3 % in ten cycles by using NaOH (*Bajpai and Chaudhuri, 1999*). The recovery of arsenic from iron-oxide-coated sand using NaOH was found to be quite effective up to 80–87% (*Thirunavukkarasu et al., 2003*) and up to 100 % from biomass (*Kamala et al., 2005*). By comparing with the several researches, it is found that heavy metal(s) from chemical adsorbents were regenerated in most of the cases using alkalis (mostly NaOH), i.e. iron-oxide-coated sand, manganese dioxide-coated sand, nano-zerovalent iron, Fe(III) oxide/hydroxide nanoparticle-based agglomerate suspension, and magnetic wheat straw (*Lata et al., 2015*).

2.6 Arsenic removal by iron oxide and iron oxide impregnated adsorbent

Gupta *et al.* (2005) showed that adsorption of arsenic (III) by using iron oxide coated sand in batch and column have been found that adsorption data showed good fit to Langmuir isotherm models at pH 7.5 in 2 hours. Adsorption capacity of iron oxide coated sand (28.57 $\mu\text{g/g}$) is more than virgin sand (5.63 $\mu\text{g/g}$) and the optimum efficiency in arsenic removal is 99 percent at adsorbent dose 20 g/L with the initial concentration of arsenic 400 $\mu\text{g/g}$ which can remove less than 24 $\mu\text{g/L}$.

Prasenjit Mondal *et al.* (2007) presented that Fe(III) impregnated granular activated carbon (GAC-Fe) was investigated for removal of arsenic, iron and manganese from groundwater. Under the experimental condition at 30°C, when GAC-Fe is used, the optimum removal of As(T), As(III), As(V), Fe and Mn are 95.5%, 93%, 98%, 100% and 41%, respectively. For GAC these values are 56%, 41%, 71%, 99% and 98%. The maximum removal of arsenite (As(III)) and arsenate (As(V)) were found in 9-11 and 5-7 of pH range, respectively. The adsorbent dosage and its particle size for both GAC and CAC-Fe were 30 g/L and 125-150 μm with the 200 ppb as the initial arsenic concentration.

Zhang *et al.* (2007) Synthesized iron oxide/activated carbon (FeO/AC) which modify the coal based activated carbon (AC) mesh size of 12 x 40 for arsenic removal in batch and column adsorption experiments. Batch and column adsorption studies revealed that FeO/AC and virgin activated carbon were effective in removing arsenic but FeO/AC is higher than virgin activated carbon at the rate of 99.1%. Column adsorption experiments with FeO/AC showed that the arsenic could be removed to below 0.01 mg/L with 1250 mL empty bed volume when influent concentration was 0.5 mg/L. The Langmuir isotherm adsorption equation well describes the experiment adsorption isotherm.

Liu *et al.* (2010) demonstrated that arsenate removal by using Fe₃O₄ loaded activated carbon (MY) prepared from waste biomass which exhibited high surface area of 349 m²/g with pore volume of 0.20 cm³/g and 39 wt.% of iron contents

showed an excellent adsorption capability for arsenate with a maximum adsorption capacity of 204.2 mg/g at pH 8.0 with the initial arsenate concentration of 40 mg/L and the adsorption process followed the Freundlich isotherm model well.

Chammui *et al.* (2014) stated that the 75 μm size of the Leonardite char carbonized at 450°C were carried out in a batch system with As(III) and As(V) at initial concentration of 10 mg/L. They found that it had the maximum removal of arsenic (III) and arsenic (V) was close to 100% (less than 0.002 mg/L) at pH 7 and the equilibrium contact time were 3 hours. The adsorption data presented fit well to both Langmuir and Freundlich isotherm. The present of competing anions (NO_3^- , Cl^- and SO_4^{2-}) with an initial As(III) or As(V) concentration of 5.0 mg/L showed that the adsorption of As(III) and As(V) slightly decreased with SO_4^{2-} , but NO_3^- and Cl^- have only a small effect.

Tuna *et al.* (2013) reported that iron (oxy-hydr)oxides loaded apricot stone based activated carbon were synthesized by precipitation method has been successful in arsenate removal. The adsorption experiments were carried out using batch equilibrium techniques with different pH level, initial arsenate (As(V)) concentration and temperature. Arsenate (As(V)) adsorption capacities of IAC, IAC-Fe(II) and IACFe(III) were found to be 15.00%, 98.34% and 99.05% of the arsenate (As(V)) removal efficiency, respectively. IAC-Fe(II) needed more adsorption time than IAC-Fe(III). The equilibrium data for both hybrid adsorbent performed well to Freundlich and Dubinin-Radushkevich model, demonstrating that arsenate (As(V)) adsorption onto hybrid adsorbents takes place on multi-layer.

CHAPTER 3

METHODOLOGY

This research conducted laboratory-scale experiments at the department of environmental engineering in Chulalongkorn University. Details of the experiments are described below.

3.1 Research overview

In this research, the experiment was divided into 13 stages:

1. Preparation of equipment and chemical reagent.
2. Preparation of iron oxide coated activated carbons using powdered activated carbon and granular activated carbon.
3. Study on the characterization of the adsorbents.
4. Preparation of synthetic arsenate-contaminated water.
5. Study on the effect of solution pH on arsenate adsorption onto adsorbents.
6. Study on the effect of contact time on arsenate adsorption onto adsorbents.
7. Study on the effect of adsorbent dosage on arsenate adsorption onto adsorbents.
8. Study on the effect of ionic strength on arsenate adsorption onto adsorbents.
9. Study on the effect of coexisting ions on arsenate adsorption onto adsorbents.
10. Comparison of the adsorbents based on the arsenate adsorption capacity was done to choose the best adsorbent to make the column experiment.
11. Study on the arsenate adsorption of the column by breakthrough curve.
12. Regeneration of iron oxide coated granular activated carbon.
13. Evaluation the cost of treatment and summary the experiment.

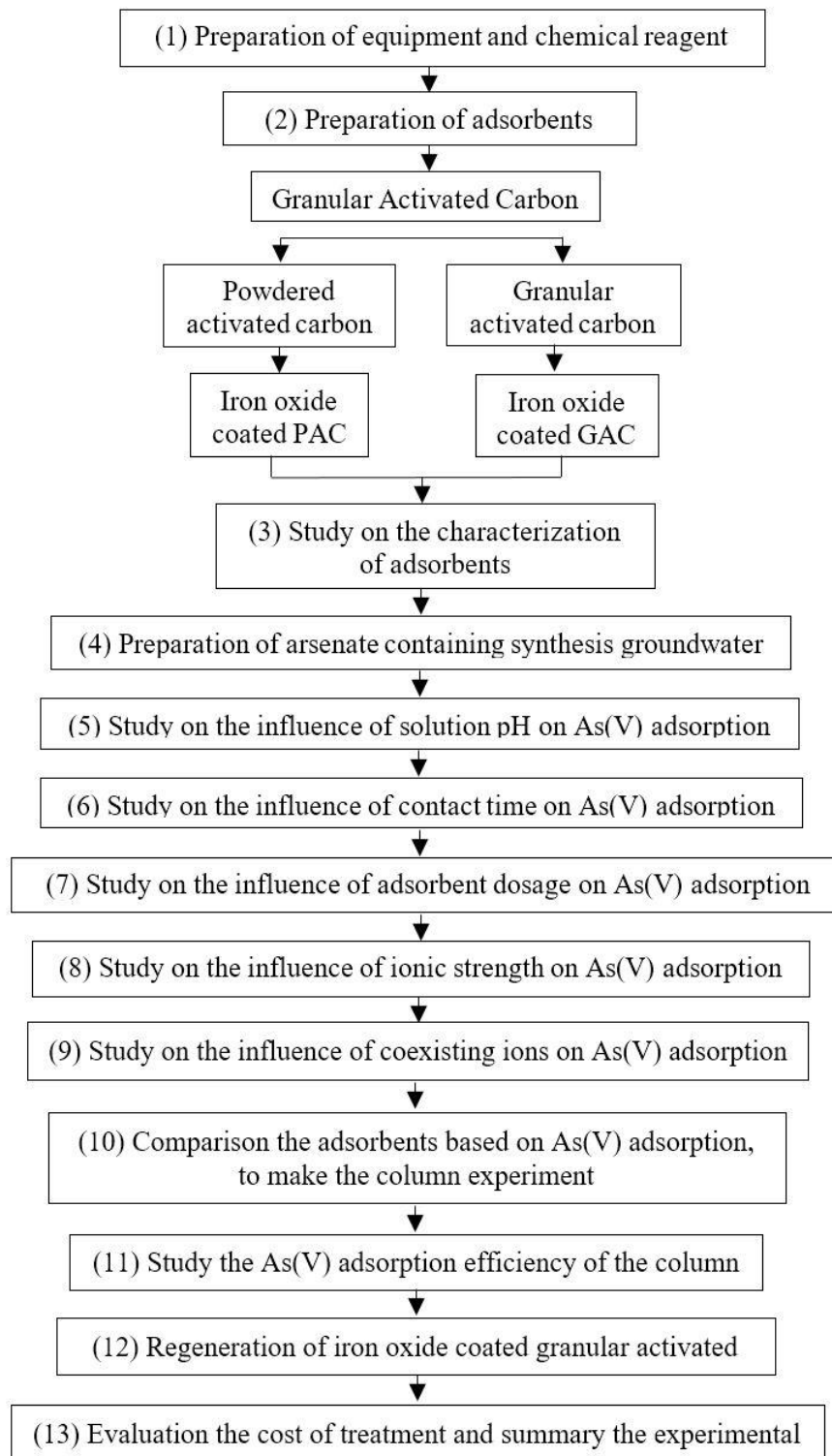


Figure 3.1 Experiment procedures diagram

3.2 Equipment and chemical reagents

3.2.1 Equipment and Tool for performing arsenate adsorption

- 250 mL glass bottles
- Centrifuge tube 50 mL
- Volumetric flasks
- Pipettes
- Precision balance
- Orbital shaker
- Convective oven
- Desiccator
- pH meter
- Solvent filtration apparatus 1L
- Syringe filter PTFE 0.45 μm (Whatman™)
- 0.45 μm mixed cellulose membrane filter with grid – sterile (Whatman™ 7141-104)
- Vacuum pump
- Scanning Electron Microscope (SEM)
- Energy X-ray Spectroscopy (EDS)
- Specific surface area analyzer (Pore Distribution Analyzer by Gas Adsorption Method NOVA4200e (BET multipoint method))
- Inductively Couple Plasma – Optical Emission Spectroscopy (ICP-OES).

3.2.2 Chemical reagent

All chemicals used in this research are of reagent grade from ROONGSUB CHEMICAL LTD., PART

- Deionized water (18 M Ω cm) was used to prepare all solutions.
- Ferrous chloride solution (FeCl₂.4H₂O) was used to coat on activated carbons.

- Sodium arsenate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$) is used to prepare the arsenate-contaminated synthetic water.
- Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were used to adjust the pH.
- Ferrous sulfate (FeSO_4) was used to prepare the coexisting ion, i.e. SO_4^{2-} , in synthesis arsenate-contaminated water.
- Arsenate standard solution (1000 $\mu\text{g}/\text{mL}$ in 2% nitric acid, Ultra Scientific certified) was used to prepare the calibration curve.

3.3 Analytical Parameters

3.3.1 pH measurement

The pH in the arsenate synthetic water samples was measured by pH probe meters (FiveEasy™ F20, METTLER TOLEDO) before and after adsorption.

3.3.2 Arsenate Concentration

Arsenate concentration (mg/L) can be measured by Inductively Couple Plasma Optical Emission Spectrometry (ICP-OES) with the standard calibration curve in range of 0.01 - 10 mg/L as total arsenic, in accordance with US EPA Method 6020.

3.3.3 Arsenate adsorption efficiency (E(%))

Arsenate adsorption efficiency (E(%)) represents the performance of the adsorption process in the reactor. Adsorption efficiency is defined from the ratio between the initial concentration and the final concentration of arsenate in the synthetic arsenate contaminated water. The arsenate adsorption efficiency can be determined by the equation below:

$$E = \frac{C_0 - C_e}{C_0} \times 100 \quad \text{Eq. 3.1}$$

where: E is the arsenate adsorption efficiency (%), C_0 is the initial concentration of arsenate (mg/L), C_e is the final concentration of arsenate (mg/L).

3.3.4 Arsenate adsorption capacity

Arsenate adsorption capacity (mg/g) is defined from the ratio between the concentration of arsenate removed which can be calculated from the initial concentration of arsenate minus the final concentration of arsenate in the arsenate contaminated synthetic water (mg/L) and the adsorbent dose (g/L). The arsenate adsorption capacity can be determined by the equation below:

$$q_e = \frac{C_0 - C_e}{M} \times V \quad \text{Eq. 3.2}$$

where: q_e is the adsorption capacity (mg/g), C_0 is the initial concentration of arsenate (mg/L), C_e is the final concentration of arsenate (mg/L), V is the volume of solution (L) and M is mass of adsorbent (g).

3.4 Preparation of iron oxide coated activated carbon

Two types of activated carbons, used in this research i.e. powder activated carbon and granular activated carbon, were prepared as follows (*Figure 3.2*).

- Granular activated carbons were thoroughly washed using deionized water (DI) to clean all impurities and dust until washed water appeared colorless
- Granular activated carbons were dried in a convective oven overnight at 105°C and stored in a desiccator until use.
- Granular activated carbons were ground by a LABORATORY DISC MILL (KAWASAKI HEAVY INDUSTRIES, LTD) to generate powdered activated carbon.
- Both activated carbons were sieved to determine the size of granular and powdered activated carbon.
- 30 grams of each activated carbons (i.g. PAC and GAC) was added into 250 mL glass bottles, filled with 0.5 M ferrous chloride solution headspace-free to avoid ferrous oxidation and precipitation.

- The bottles were placed on an orbital shaker for 24 hours with a shaking speed of 200 rpm at the room temperature ($25^{\circ}\text{C} \pm 2$) to achieve fully penetration and saturation of ferrous in activated carbon pores.
- After 24 hours of shaker, the activated carbons were separated from the ferrous solution and thoroughly washed with deionized water ($18 \text{ M}\Omega \text{ cm}$) until the washed water appeared colorless. Then, ACs were placed in a convective oven at 105°C for 10 hours. In this step, ferrous was oxidized to ferric making it less soluble at the same time when activated carbons were dried. This step was repeated several times ensuring in more iron oxide coated on activated carbons.
- Iron oxide coated activated carbons were kept in a desiccator until use as the effective adsorbents to adsorb arsenate from contaminated groundwater.



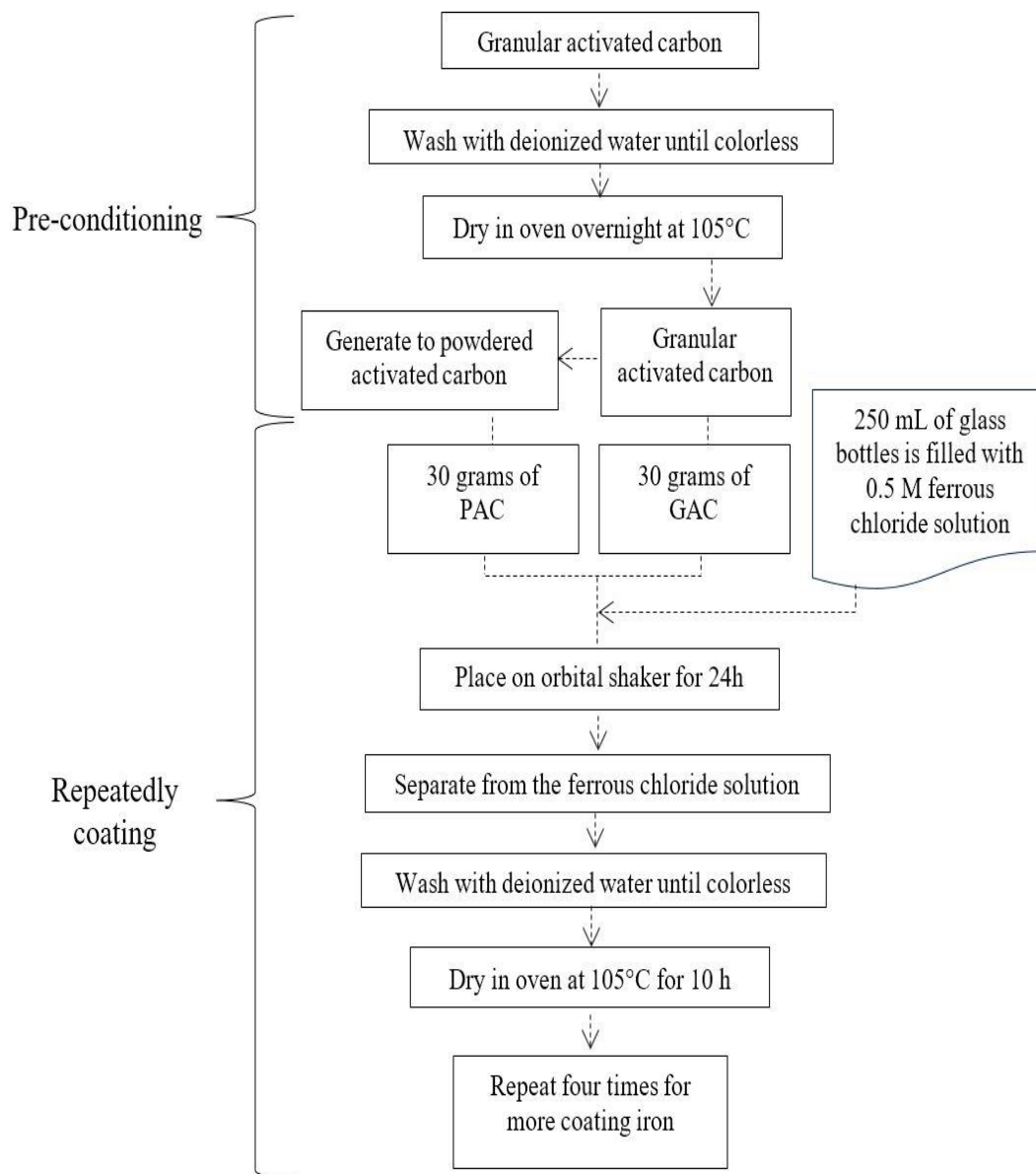


Figure 3.2 Coating of iron oxide on powdered/granular activated carbon

3.5 Characterization of iron oxide coated activated carbon

By examining the physical and chemical properties of 4 types of adsorbents:

- Virgin powdered activated carbon
- Virgin granular activated carbon
- Iron oxide coated powdered activated carbon
- Iron oxide coated granular activated carbon

Table 3.1 Physical and chemical properties and analysis method

	Analytical
<u>Physical property</u>	
<i>Point of zero charge</i>	<i>pH drift method</i>
<i>Structure characterization</i>	<i>Scanning Electron Microscopy</i>
<i>Specific surface area</i>	<i>Gas adsorption method (BET multipoint method) using Pore Distribution Analyzer</i>
<u>Chemical property</u>	
<i>Chemical element on surface</i>	<i>Energy Dispersive X-ray Spectroscopy</i>

3.5.1 Point of zero charge

The point of zero charge (pH_{PZC}) of virgin activated carbon and iron oxide coated activated carbon were determined by pH drift method. 50 mL of solution containing of 1 mg/L of arsenate (As(V)) concentration with 5 g/L of adsorbents were shaken at 200 rpm for 24 hours at the room temperature (25 ± 2). The pH was varied from 2 to 10, sodium hydroxide (NaOH) and hydrochloric acid (HCl) were used to adjust the initial pH. The initial pH and final pH were measured and plotted the relation between the initial pH and final pH.

3.5.2 Structure characterization

The structural of adsorbents were observed by Scanning Electron Microscopy under different magnification (Hitachi S-4800) at Analytical and Testing Service Center, Petroleum and Petrochemical College, Chulalongkorn University.

3.5.3 Specific surface area

The specific surface area and pore size distribution of adsorbents were measured by Pore Distribution Analyzer (BET multipoint method) at Analytical and Testing Service Center, Petroleum and Petrochemical College, Chulalongkorn University.

3.5.4 Chemical element on surface

The chemical element on surface was measured by Energy Dispersive X-ray spectroscopy (EDX) at Analytical and Testing Service Center, Petroleum and Petrochemical College, Chulalongkorn University.

3.6 Preparation of arsenate contaminated synthesis water

Synthesis arsenate contaminated water is prepared by diluting sodium arsenate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$) at the initial concentration of 1.0 mg /L as AsO_4 in deionized water (18 M Ω cm).

3.7 Factors affecting the arsenate adsorption

3.7.1 The effects of solution pH on arsenate adsorption

pH is one of the most important parameters that affect the adsorption of arsenate in liquid phase and ionization of the surface functional groups of adsorbents. Hence, the pH value of the solution is required to investigate, as follows:

- Preparing of synthesis arsenate contaminated water of 5000 mL with the initial concentration of 1 mg/L as AsO_4 ; sodium hydroxide (NaOH) and hydrochloric acid (HCl) were used to adjust the pH: i.e. 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0.
- Transferring four types of adsorbents i.e., PAC, GAC, Fe-PAC and Fe-GAC with a dose of 5.0 g/L to 50 mL centrifuge tube (9 tubes/adsorbent).
- The centrifuge tubes were shaken on an orbital shaker at 200 rpm, 24 hours at the room temperature ($25^\circ\text{C} \pm 2$).
- The samples were filtered through a 0.45 μm membrane filter and pH of the solutions were measured.
- The samples were analyzed by Inductively Couple Plasma Optical Emission Spectrometry (ICP-OES).to measure the final concentration of arsenate.
- The arsenate removal efficiency and the amount of arsenate adsorbed on the adsorbent were calculated by Eq. 3.1 and 3.2, respectively.
- Plotting a graph showing the relation between pH and arsenate removal efficiency (%).

Table 3.2 Parameter measurement for the optimum pH

<i>Variable</i>	<i>Parameter</i>
▪ <i>Fixed variable</i>	
- <i>Reactor</i>	<i>Batch</i>
- <i>Initial arsenate concentration</i>	<i>1.0 mg/L as AsO₄</i>
- <i>Arsenate volume</i>	<i>50 mL</i>
- <i>Contact time</i>	<i>24 hours</i>
- <i>Speed of orbital shaker</i>	<i>200 rpm</i>
- <i>Adsorbent dosage</i>	<i>5.0 g/L</i>
- <i>Temperature</i>	<i>25°C ± 2</i>
- <i>Adsorbent type</i>	<ul style="list-style-type: none"> ▪ <i>Powdered activated carbon</i> ▪ <i>Granular activated carbon</i> ▪ <i>Iron oxide coated powdered AC</i> ▪ <i>Iron oxide coated granular AC</i>
▪ <i>Independent variable</i>	
- <i>pH</i>	<i>2.0 to 10.0</i>
▪ <i>Dependent variable</i>	
- <i>Water analysis</i>	<p><i>pH after adsorption</i></p> <p><i>Residual arsenate (mg/L)</i></p>
- <i>Removal efficiency</i>	<i>Percentage of arsenate adsorbed (%)</i>
- <i>Analysis result</i>	<i>Optimum pH</i>

3.7.2 The effect of contact time on the arsenate adsorption

Contact time is the effective factors in batch adsorption experiment that affects the adsorption of arsenate in liquid phase. To investigate the effect of contact time on arsenate adsorption, as follows:

- Preparing of synthesis arsenate contaminated water of 6000 mL with the initial concentration of 1 mg/L as AsO_4 , sodium hydroxide (NaOH) and hydrochloric acid (HCl) were used to control the pH. The optimum pH was obtained from 3.3.4 (1) study.
- Four types of adsorbent i.e., PAC, GAC, Fe-PAC and Fe-GAC with 5.0 g/L were transferred into 50 mL centrifuge tube (10 tubes/adsorbent).
- The tubes were placed on an orbital shaker at 200 rpm, and operated for various contact time i.e. 1, 2, 4, 6, 8, 10, 12, 16, 20 and 24 hours at the room temperature ($25^\circ\text{C} \pm 2$).
- The samples were filtered through a 0.45 μm membrane filter and pHs were measured.
- The samples were analyzed by Inductively Couple Plasma Optical Emission Spectrometry (ICP-OES) to measure the final concentration of arsenate.
- The arsenate removal efficiency (%) and the amount of arsenate adsorbed on the adsorbent were calculated by Eq. 3.1 and 3.2, respectively.
- Plotting a graph showing the relation between contact time (h) and arsenate removal efficiency (%).

Table 3.3 Parameter measurement for the optimum contact time

Variable	Parameter
▪ <u>Fixed variable</u>	
- Reactor	Batch
- Initial arsenate concentration	1.0 mg/L as AsO ₄
- Arsenate volume	50 mL
- pH	*obtained from 3.3.4 (1) study
- Speed of orbital shaker	200 rpm
- Adsorbent dosage	5.0 g/L
- Temperature	25°C ± 2
- Adsorbent type	<ul style="list-style-type: none"> ▪ Powdered activated carbon ▪ Granular activated carbon ▪ Iron oxide coated powdered AC ▪ Iron oxide coated granular AC
▪ <u>Independent variable</u>	
- Contact time	1 to 24 hours
▪ <u>Dependent variable</u>	
- Water analysis	pH after adsorption Residual arsenate (mg/L)
- Removal efficiency	Percentage of arsenate adsorbed (%)
- Analysis result	Optimum contact time

3.7.3 The effect of adsorbent dosage on the arsenate adsorption

Adsorbent dosage is one of the most important parameters for adsorption process that affects adsorption efficiency. To investigate the effect of adsorbent dosage on arsenate adsorption, as follows:

- Preparing of synthesis arsenate contaminated water of 4000 mL with the initial concentration of 1 mg/L as AsO_4 , sodium hydroxide (NaOH) and hydrochloric acid (HCl) were used to adjust the pHs. The optimum pH was obtained from 3.3.4 (1) study.
- Four types of adsorbents, i.e., PAC, GAC, Fe-PAC and Fe-GAC, containing various amount of adsorbent i.e. 1.0, 2.0, 3.0, 4.0, 5.0 and 6.0 g/L, were transferred to 50 mL centrifuge tube (6 tubes/adsorbent).
- The centrifuge tubes were placed on an orbital shaker at 200 rpm, with the optimum contact time was obtained from 3.3.4 (2) study at the room temperature ($25^\circ\text{C} \pm 2$).
- The samples were filtered through a $0.45 \mu\text{m}$ membrane filter and pHs were measured.
- The samples were analyzed by Inductively Couple Plasma Optical Emission Spectrometry (ICP-OES) to measure the final concentration of arsenate
- The arsenate removal efficiency and the amount of arsenate adsorbed on the adsorbent were calculated by Eq. 3.1 and 3.2, respectively.
- Plotting a graph showing the relation between adsorbent dosage (g/L) and arsenate removal efficiency (%).

Table 3.4 Parameter measurement for the optimum adsorbent dosage

<i>Variable</i>	<i>Parameter</i>
▪ <u>Fixed variable</u>	
- Reactor	Batch
- Initial arsenate concentration	1.0 mg/L as AsO ₄
- Arsenate volume	50 mL
- pH	*obtained from 3.3.4 (1) study
- contact time	*obtained from 3.3.4 (2) study
- Speed of orbital shaker	200 rpm
- Adsorbent dosage	5.0 g/L
- Temperature	25°C ± 2
- Adsorbent type	<ul style="list-style-type: none"> ▪ Powdered activated carbon ▪ Granular activated carbon ▪ Iron oxide coated powdered AC ▪ Iron oxide coated granular AC
▪ <u>Independent variable</u>	
- Adsorbent dosage	1.0 to 6.0 g/L
▪ <u>Dependent variable</u>	
- Water analysis	pH after adsorbed Residual arsenate (mg/L)
- Removal efficiency	Percentage of arsenate adsorbed (%)
- Analysis result	Optimum adsorbent dosage

3.7.4 The effect of the ionic strength on the arsenate adsorption

Preparing of synthesis arsenate contaminated water of 2000 mL with the initial concentration of 1 mg/L as AsO_4 , sodium hydroxide (NaOH) and hydrochloric acid (HCl) were used to adjust solution pHs. The optimum pH was obtained from 3.3.4 (1) study, containing varied amounts of NaCl (0, 0.01 and 0.1 M) as ionic strength.

- Transferring 4 types of adsorbents, i.e., PAC, GAC, Fe-PAC and Fe-GAC to 50 mL of centrifuge tube. The optimum of adsorbent dosage was obtained from 3.3.4 (3).
- The centrifuge tubes were placed on an orbital shaker at 200 rpm, with the optimum contact time that was obtained from 3.3.4 (2) at the room temperature ($25^\circ\text{C} \pm 2$).
- The samples were filtered through a $0.45 \mu\text{m}$ membrane filter and pHs were measured.
- The samples were analyzed by Inductively Couple Plasma Optical Emission Spectrometry (ICP-OES) to measure the final concentration of arsenate
- The arsenate removal efficiency and the amount of arsenate adsorbed on the adsorbent were calculated by Equation 3.1 and 3.2, respectively.
- Plotting a graph showing the relation between ionic strength and percentage of arsenate adsorbed (%).

Table 3.5 Parameter measurement for the optimum ionic strength

Variable	Parameter
▪ <u>Fixed variable</u>	
- Reactor	Batch
- Initial arsenate concentration	1.0 mg/L as AsO ₄
- Arsenate volume	50 mL
- pH	*obtained from 3.3.4 (1) study
- Contact time	*obtained from 3.3.4 (2) study
- Adsorbent dosage	*obtained from 3.3.4 (3) study
- Speed of orbital shaker	200 rpm
- Adsorbent dosage	5.0 g/L
- Temperature	25°C ± 2
- Adsorbent type	<ul style="list-style-type: none"> ▪ Powdered activated carbon ▪ Granular activated carbon ▪ Iron oxide coated powdered AC ▪ Iron oxide coated granular AC
▪ <u>Independent variable</u>	
- Ionic strength	0.01 M and 0.1 M as NaCl
▪ <u>Dependent variable</u>	
- Water analysis	pH after adsorption Residual arsenate (mg/L)
- Removal efficiency	Percentage of arsenate adsorbed (%)
- Analysis result	Optimum ionic strength

3.7.5 The effect of coexisting ions on arsenate adsorption

Numerous anionic components might exist in groundwater and might compete with arsenic for adsorption sites (Yao *et al.*, 2014) Among the major coexisting anionic components, iron is generally present in groundwater probably inhibiting the arsenic removal.

- Preparing of synthesis arsenate contaminated water of 1000 mL with the initial concentration of 1 mg/L as AsO_4 with the coexisting ions (sulfate ion) with concentration of 5 mg/L. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were used to adjust the solution pH to the optimum of pH that was obtained from 3.3.4 (1) study.
- Four types of adsorbents, i.e., PAC, GAC, Fe-PAC and Fe-GAC were transferred to 50 mL of centrifuge tube. The optimum of adsorbent dosage was obtained from 3.3.4 (3).
- The centrifuge tubes were placed on an orbital shaker at 200 rpm, with the optimum contact time that was obtained from 3.3.4 (2) at the room temperature ($25^\circ\text{C} \pm 2$).
- The samples were filtered through a $0.45 \mu\text{m}$ membrane filter and pHs were measured.
- The samples were analyzed by Inductively Couple Plasma Optical Emission Spectrometry (ICP-OES) to measure the final concentration of arsenate.
- The arsenate removal efficiency and the amount of arsenate adsorbed on the adsorbent were calculated by Equation 3.1 and 3.2, respectively.
- Comparison the percentage of arsenate adsorbed (%) between without and with adding coexisting iron.

Table 3.6 Parameter measurement for the co-existing ion

Variable	Parameter
▪ <u>Fixed variable</u>	
- Reactor	Batch
- Initial arsenate concentration	1.0 mg/L as AsO ₄
- Arsenate volume	50 mL
- pH	*obtained from 3.3.4 (1) study
- Contact time	*obtained from 3.3.4 (2) study
- Adsorbent dosage	*obtained from 3.3.4 (3) study
- Ionic strength	* obtained from 3.3.4 (4) study
- Speed of orbital shaker	200 rpm
- Adsorbent dosage	5.0 g/L
- Temperature	25°C ± 2
- Adsorbent type	<ul style="list-style-type: none"> ▪ Powdered activated carbon ▪ Granular activated carbon ▪ Iron oxide coated powdered AC ▪ Iron oxide coated granular AC
▪ <u>Independent variable</u>	
- Coexisting ion	5.0 mg/L as FeSO ₄
▪ <u>Dependent variable</u>	
- Water analysis	pH after adsorption Residual arsenate (mg/L)
- Removal efficiency	Percentage of arsenate adsorbed (%)

3.8 Rapid Lab-Scale Column adsorption

Continuous flow adsorption study was conducted in a column made of acrylic tube having an inner diameter of 20 mm and height of 30 mm. The column was packed with 5.0 g of iron oxide coated granular activated carbon (Fe-GAC). Steel grating and 0.45 μm membrane filters were placed at the top and bottom of the column to prevent the wastage of adsorbent. A peristaltic pump (Masterflex[®] L/S Model 77202-60) was used to suck the arsenate solution of 1.0 mg/L as AsO_4 (at pH 5.0 and room temperature $25^\circ\text{C} \pm 2$) upward through the column at a constant flowrate of 1.0 mL/min. The effluent samples were collected at specified time and measured for the remaining arsenate concentration using ICP-OES. C/C_0 and t were used to plot the breakthrough curve.

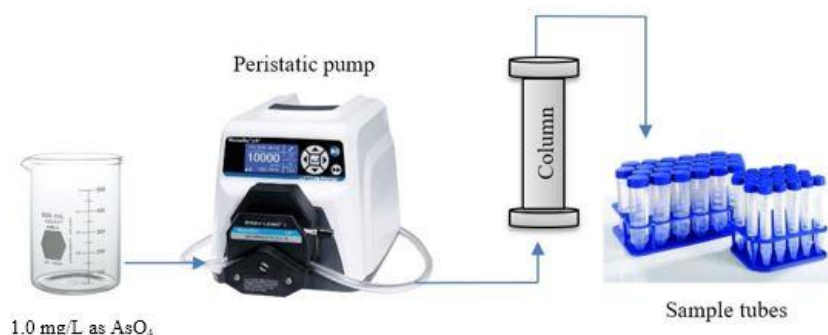


Figure 3.3 Rapid Lab-Scale Column adsorption system

3.9 Regeneration of iron oxide coated activated carbon in column test

In order for the adsorption process to be viable, the regeneration and reuse of the adsorbent are required. The regeneration of iron oxide coated granular activated carbon was carried out by using 0.1M Sodium hydroxide (NaOH) with flow rate 25 mL/min in an upward direction through the column for 45 minutes (Nonlaphan., 2011). After regeneration, the adsorbent was reconditioned using deionized water at the same flow rate 25 mL/min to remove the excess NaOH contained in the adsorbents and thus lower the pH (7 ± 1). The iron content in the adsorbent was

assumed to remain unaltered after regeneration (Kundu and Gupta, 2005). Following rinsing, iron oxide coated granular activated carbon (Fe-GAC) was ready for the next adsorption cycle.

3.10 Cost treatment analysis

An empirical approach was used to analyze the treatment cost of virgin activated carbon and iron oxide coated activated carbon. This approach was explained the capital per unit of adsorbent dosage.

$$\text{Cost}/100\text{g} = \text{Activated carbon} + \text{Chemical used}$$



CHAPTER 4

ADSORBENT CHARACTERIZATION AND ADSORPTION OF ARSENATE

This chapter presents the experimental and analysis results covering three main objectives including (i) the adsorbent development and its characterization, (ii) the impact factor on arsenate adsorption and (iii) the comparison of arsenate adsorption among different adsorbents. In this research, sodium arsenate dibasic heptahydrate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$) was used for preparing the synthetic arsenate-contaminated groundwater with the arsenate concentration of 1.0 mg AsO_4/L and four types of adsorbents: (i) virgin powdered activated carbon (PAC), (ii) virgin granular activated carbon (GAC), (iii) iron oxide coated powdered activated carbon (Fe-PAC) and (iv) iron oxide coated granular activated carbon (Fe-GAC) were used in this experiment. The results are divided into four main parts:

- ❖ The physical and chemical properties of adsorbents
 - The specific surface area analysis of adsorbents by BET method
 - The structural analysis of adsorbents by Scanning electron microscopy
 - The chemical composition analysis of adsorbent by Energy Dispersive X-ray spectroscopy
- ❖ Batch adsorption experiment to investigate effects of following parameters on the arsenate (As(V)) adsorption:
 - Equilibrium solution pH
 - Contact time
 - Adsorbent dosage
 - Ionic strength
 - Coexisting ions
- ❖ Rapid Lab-scale Column Test and regeneration
 - The adsorption efficiency of iron oxide coated granular activated carbon

- Modelling of analytical result on the arsenate (As(V)) adsorption onto iron oxide coated granular activated carbon (Thomas model)
- The regeneration of iron oxide coated granular activated carbon
- ❖ Cost analysis
 - The comparison of the cost and its efficiency of iron oxide coated granular activated carbon on the arsenate (As(V)) adsorption

RESULTS AND DISCUSSION

4.1 The physical and chemical properties of adsorbents

4.1.1 The point of zero charge

The functional groups and pH_{PZC} of the surface of an adsorbent are important because they indicate the acidity/basicity of the adsorbent and the net surface charge of the carbon in solution, respectively (*Al-Degs et al., 2008*).

The point of zero charge of virgin activated carbon and iron oxide coated activated carbon were determined by pH drift method. The pH_{PZC} is the point where the curve of pH_{final} vs $\text{pH}_{\text{initial}}$ intersects the line $\text{pH}_{\text{initial}} = \text{pH}_{\text{final}}$. The pH_{PZC} of virgin activated carbon and iron oxide coated activated carbon were found to be 6.7 and 5.5, respectively, as shown in *Figure 4.1* & *Figure 4.2*. Below the pH_{PZC} , the surface of adsorbent has a net positive charge and anion adsorption occurs. Furthermore, above the pH_{PZC} adsorbent surface is negatively charged, and has affinity to cation (*Tuna et al., 2013*).

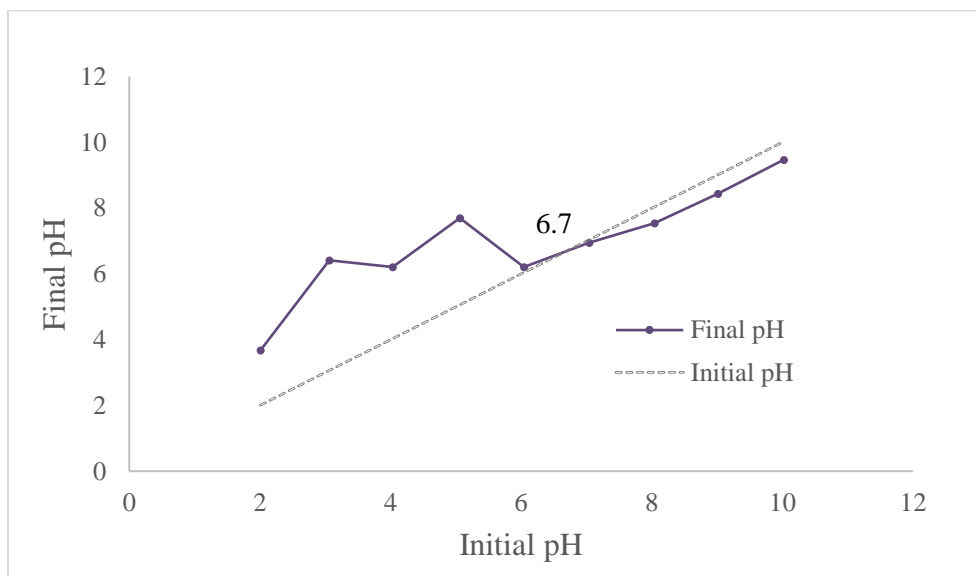


Figure 4.1 The point zero charge of virgin activated carbon

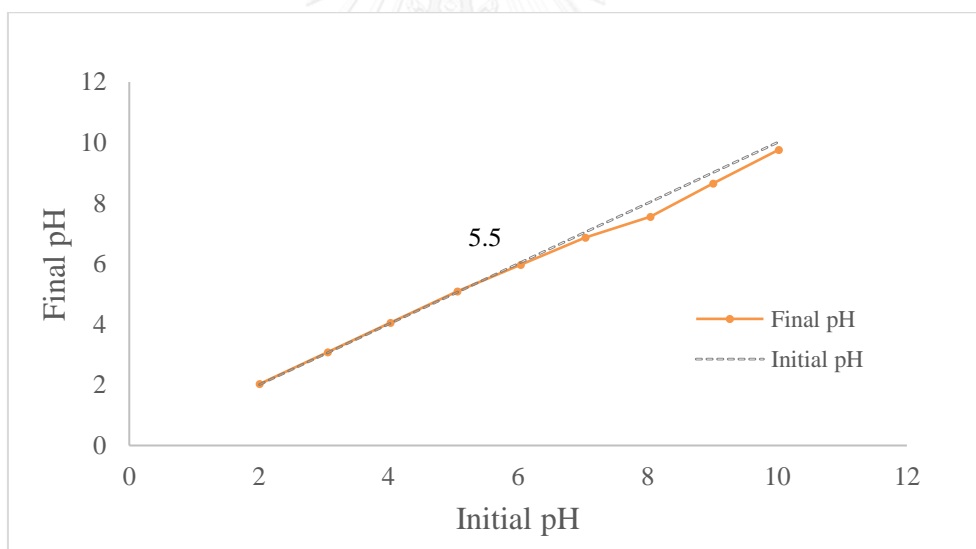


Figure 4.2 The point zero charge of iron oxide coated activated carbon

4.1.2 The specific surface area analysis of adsorbent by BET method

The microstructure changes of virgin activated carbons and iron oxide coated activated carbons were listed in *Table 4.1*. As shown in *Table 4.1*, virgin powdered activated carbon and virgin granular activated carbon had similar surface area (S_{BET}) due to virgin granular activated carbon has been grounded by a cup mill to generate

virgin powdered activated carbon. This demonstrates that grinding does not change the physical property of the carbon surfaces and thereby the difference in the adsorption behaviors could be ascribed to the different particle sizes between PAC and GAC. Powdered and granular activated carbon were measured by shaking a sample of activated carbon through a defined series of sieves. It was found that granular activated carbon is 20x40 US mesh (effective size 0.42 – 0.85 mm) and powdered activated carbon has a very small particle size, less than 0.075 mm (US Mesh 200). Total pore volumes of virgin powdered activated carbon and virgin granular activated carbon were decreased after coating with iron oxide, which decreased from 0.54 to 0.43 and 0.56 to 0.53, respectively. The presence of the iron oxide coating can cause a decrease in the surface area and microporous volume compared to virgin powdered/granular activated carbon.

Table 4.1 Microstructure of virgin and iron oxide coated powdered/granular activated carbon

<i>Adsorbent</i>	<i>S_{BET}</i> <i>(m²/g)</i>	<i>Average pore</i> <i>diameter (Å)</i>	<i>Total pore volume</i> <i>(cm³/g)</i>
<i>Virgin powdered activated carbon</i>	768	28.	0.54
<i>Virgin granular activated carbon</i>	766	29	0.56
<i>Iron oxide coated powdered activated carbon</i>	561	31	0.43
<i>Iron oxide coated granular activated carbon</i>	722	30	0.54

4.1.3 The structural analysis of adsorbents by Scanning electron microscopy

Virgin powdered activated carbon (PAC), virgin granular activated carbon (GAC), iron oxide coated powdered activated carbon (Fe-PAC) and iron oxide coated granular activated carbon (Fe-GAC) were analyzed by Scanning Electron Microscopy (Hitachi S-4800). Between PAC and GAC, it can be noticed that both products had a very dense structure and big holes as pointed out by arrow in *Figure 4.3*. Whereas Fe-PAC and Fe-GAC, there are few macropores in activated carbon and smooth surface, indicating that iron oxide particles covered on the activated carbon surfaces.

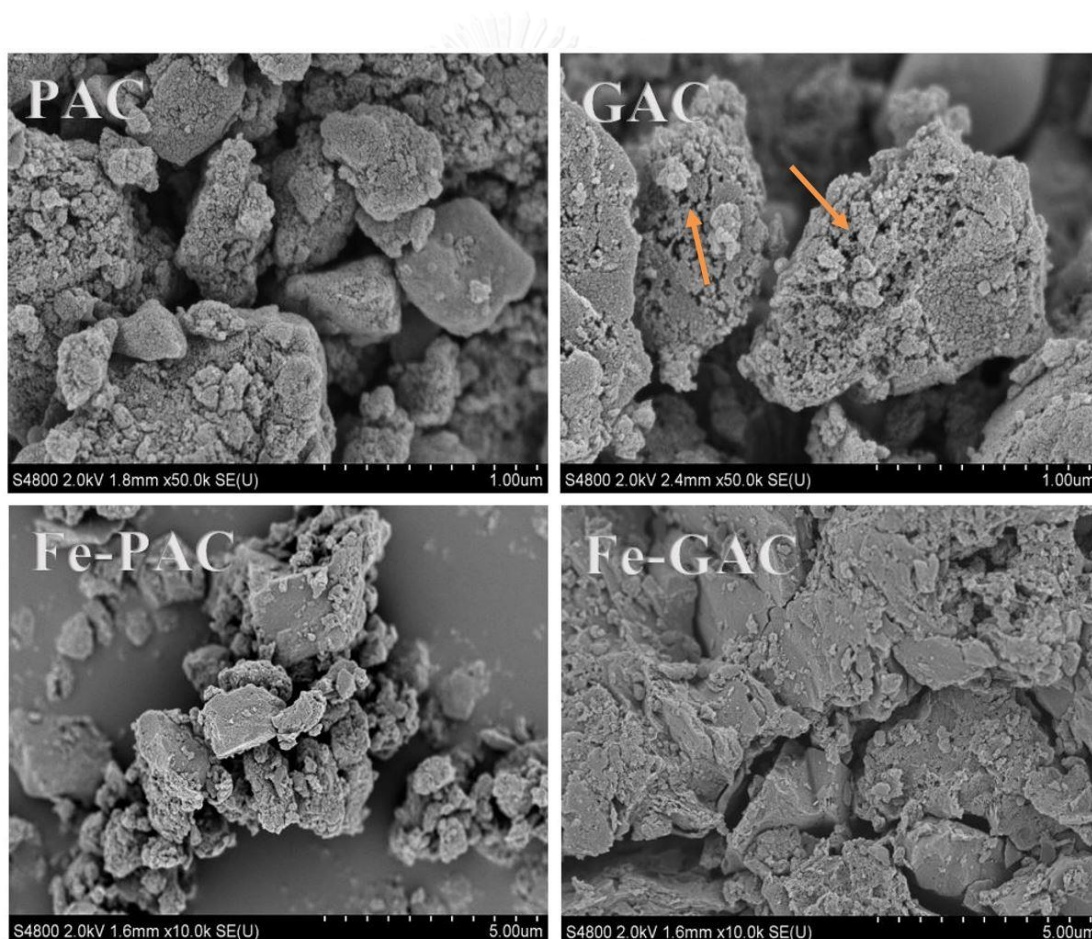


Figure 4.3 SEM micrographs of virgin powdered activated carbon, virgin granular activated carbon, Iron oxide coated powdered activated carbon and iron oxide coated granular activated carbon.

4.1.4 The chemical composition analysis of adsorbent by Energy Dispersive X-ray spectroscopy

Virgin powdered/granular activated carbon and iron oxide coated powdered/granular activated carbon were analyzed by Energy Dispersive X-ray spectroscopy (5 spots/adsorbent). The results were summarized in Table 4.2. As shown in Table 4.2, the Fe percentages were increased after coating with iron oxide from 0.15% to 3.73% and 0.58% to 4.21% for Fe-PAC and Fe-GAC, respectively. It is indicated that iron oxide coating on powdered/granular activated carbon were completely impregnated.

Table 4.2 Element analyzing of adsorbent by Energy Dispersive X-ray spectroscopy

<i>Adsorbent</i>	<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>
<i>Virgin powdered activated carbon</i>	<i>C</i>	89.69	92.94
	<i>O</i>	7.77	6.04
	<i>Al</i>	0.37	0.17
	<i>Si</i>	0.46	0.20
	<i>S</i>	1.48	0.57
	<i>CL</i>	0.09	0.03
	<i>Fe</i>	0.15	0.03
<i>Virgin granular activated carbon</i>	<i>C</i>	83.07	91.22
	<i>O</i>	3.23	2.67
	<i>Al</i>	3.52	1.72
	<i>Si</i>	5.19	2.44
	<i>S</i>	4.41	1.82
	<i>Fe</i>	0.58	0.14
	<i>Iron oxide coated powdered activated carbon</i>	<i>C</i>	71.64
<i>O</i>		13.60	11.74
<i>Al</i>		2.14	1.10
<i>Si</i>		3.55	1.75
<i>S</i>		0.89	0.38
<i>Cl</i>		4.44	1.73
<i>Fe</i>		3.73	0.92
<i>Iron oxide coated granular activated carbon</i>	<i>C</i>	73.13	84.27
	<i>O</i>	10.28	8.90
	<i>Al</i>	3.06	1.57
	<i>Si</i>	5.27	2.60
	<i>S</i>	1.24	0.53
	<i>Cl</i>	2.80	1.09
	<i>Fe</i>	4.21	1.04

4.2 The effects of the optimum factors on arsenate (As(V)) adsorption in batch experiment

4.2.1 The equilibrium solution pH

The solution pH is an important factor for all water and wastewater treatment systems. Especially in arsenate adsorption in the aqueous phase, because the arsenate species and the surface charge of iron oxide coated activated carbons in aqueous phase depend on the solution pH. Hence, the experiments were performed to investigate the effect of equilibrium pH of the solution to be treated regarding arsenate (As(V)). Constancy of the solution pH value is therefore required in order to study the effect of the pH level on the adsorption of arsenate. Arsenate adsorption on adsorbents was carried out at seven levels of pH at room temperature ($25^{\circ}\text{C} \pm 2$). *Figure 4.4* illustrates the percentage of arsenate removal as a function of pH value at pH ranging from 2.0 to 8.0.

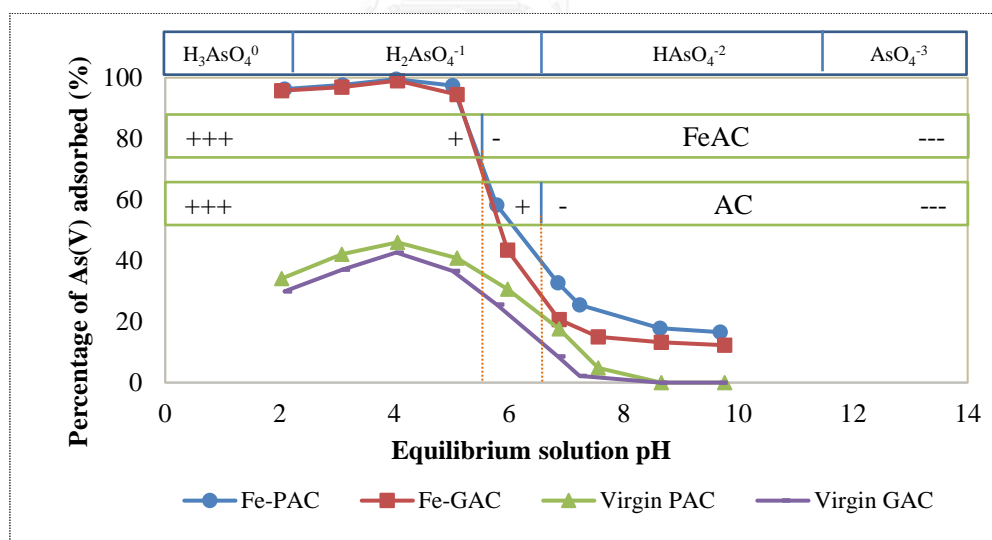


Figure 4.4 The effect of equilibrium solution pH on arsenate (As(V)) adsorption

It is evident that the arsenate (As(V)) removal firmly depends on the solution pH: i.e., arsenate adsorption decreases with the increasing pH. Moreover, it can be observed that the maximum arsenate (As(V)) adsorption capacities of virgin powdered activated carbon and virgin granular activated carbon, iron oxide coated

powdered activated carbon and iron oxide coated granular activated carbon for arsenate removal occurred at pH 2.0-5.0. The maximum arsenate (As(V)) adsorption capacity was found at lower pH as reported by several previous studies, due to the point zero charge of adsorbent and arsenate species (Gu *et al.*, 2005; P Mondal *et al.*, 2008; Oliveira *et al.*, 2002; Vitela-Rodriguez and Rangel-Mendez, 2013). At pH 4.0, adsorption capacities of V-PAC, V-GAC, Fe-PAC and Fe-GAC were 0.097, 0.090, 0.212 and 0.206 mg/g, which represented 46%, 42.67%, 97.43% and 94.50% of arsenate (As(V)) adsorbed percentage, respectively. At pH 2.2 – 6.7, the arsenate (As(V)) is in form of H_2AsO_4^- , which related to the study of Diamadopoulos *et al.* (1993), they used fly ash to remove arsenic from water and found that at pH 4 gives the best adsorption efficiency which indicated that arsenate mostly found in this research is H_2AsO_4^- as Figure 4.5.

The results shown in Figure 4.4 indicated that the iron oxide coated activated carbon adsorbents (both type: PAC and GAC) had much higher arsenate adsorption capacities than virgin activated carbon (Pattanayak *et al.*, 2000).

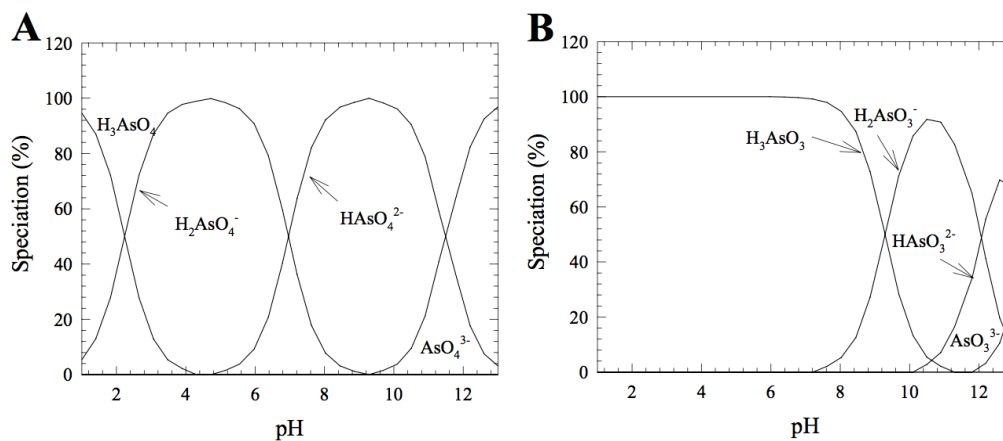


Figure 4.5 Speciation of (A) arsenate and (B) arsenite as function of pH

The highest removal efficiency had taken place at pH 4.0 (46%, 42.67%, 97.43% and 94.50%) for virgin powdered activated carbon, virgin granular activated carbon, iron oxide coated powdered activated carbon and iron oxide coated granular activated carbon, respectively. Solution pH 5.0 had selected as an optimum pH condition for further experiments because it is closely represented pH of real bearing

groundwater from Laos. Above pH 5.0 As(V) adsorption was found to be decreased. This observation could be related to the point of zero charge (PZC) of both virgin activated carbons and iron oxide coated activated carbons. The point of zero charge (pH_{PZC}) of virgin activated carbons and iron oxide coated activated carbons were found to be 6.7 and 5.5, respectively. Over the pH_{PZC} value, the surface of adsorbents is negatively charged, which could not attract the arsenate (As(V)) in form of H_2AsO_4^- that has the same charge to activated carbon surface.

4.2.2 The contact times

Contact time is the important factors for batch adsorption process. The effect of contact time on arsenate (As(V)) adsorption efficiency was shown in *Figure 4.6*. Experiment condition employed with the initial concentration of 1.0 mg AsO_4/L , solution pH 5.0, adsorbent dosage 5 g/L with shaken speed 200 rpm. The adsorption efficiency of arsenate (As(V)) onto virgin powdered activated carbon, virgin granular activated carbon, iron oxide coated powdered activated carbon and iron oxide coated granular activated carbon significantly increase at the initial adsorption phase and continuously increase at lower rate until the equilibrium was reached. The equilibrium attained after 16 hours for V-PAC, V-GAC, Fe-GAC and Fe-PAC. There was no significant change in the arsenate adsorption rates during 16 hours to 24 hours. Based on the result, 16 hours was taken as the contact time in the further adsorption experiment. Normally, the removal rate of adsorbate is rapid at the first stage, but it gradually decreases with contact time until it reaches equilibrium (*Yao et al., 2014*). The surface areas of adsorbents are available for adsorption at the first stage, and after a period of time in adsorption, the residual surface areas available for arsenate adsorption are hard to be occupied because of repulsive forces among the solute molecules on the bulk and solid phases. Similar findings were recorded by other researchers (*Gulnaz et al., 2011; Kord Mostafapour et al., 2012*).

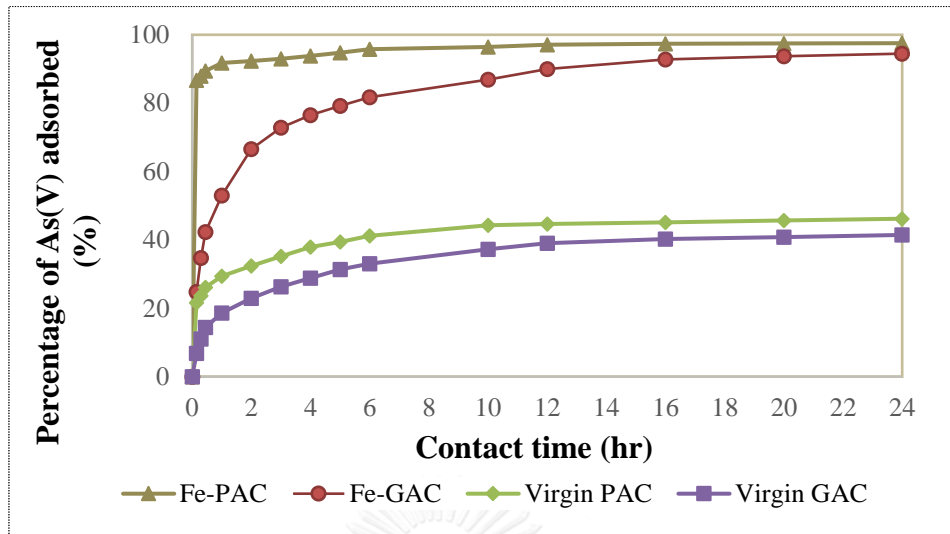


Figure 4.6 The effect of contact time on arsenate (As(V)) adsorption

4.2.3 Kinetic study on the arsenate adsorption

Figure 4.6 illustrate that the equilibrium was reached at 16 hours for all four adsorbents, which is related with percentage of arsenate (As(V)) adsorbed. For the increasing of time (<16 hours), the adsorption trend appears to be constant.

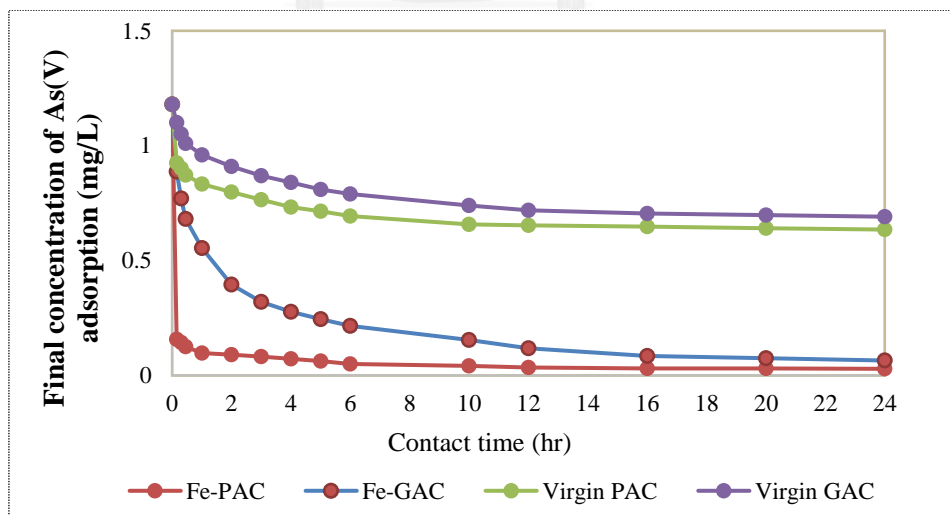


Figure 4.7 The adsorption kinetic of four types of adsorbent on arsenate adsorption

In order to investigate the mechanism of arsenate (As(V)) adsorption on four types of adsorbent, the pseudo-first order and pseudo-second order rate equation models were applied to the kinetic data. Pseudo 2nd order kinetics describes that the rate limiting step involves chemisorption which are valence forces via sharing or exchange of electron between adsorbent and adsorbate.

1. The pseudo first order kinetic equation could be derived as:

$$-dq_t/dt = k_1(q_e - q_t) \quad \text{Eq. 4.1}$$

Separating the variable in equation (4.1) gives:

$$-d(q_e - q_t)/(q_e - q_t) = k_1 \cdot dt \quad \text{Eq. 4.2}$$

Integrating both sides for the boundary condition $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = t$ gives the integrated rate law for a pseudo-first order reaction,

$$\ln(q_e - q_t) = -k_1 \cdot t + \ln q_e \quad \text{Eq. 4.3}$$

Equation (4.3) can be rearranged to obtain:

$$\ln(q_e - q_t) = \ln q_e - k_1 \cdot t \quad \text{Eq. 4.4}$$

where:

- k_1 pseudo first order kinetic constant rate (hr^{-1})
- q_e the adsorbed amount per adsorbent at equilibrium stage (mg/g)
- q_t the adsorbed amount per adsorbent at time (mg/g)
- t contact time (hr)

The kinetic constant, k_1 can be determined by plotting of $\ln(q_e - q_t)$ with t . q_e (cal) can be calculated based on slope ($1/q_e$) using Eq. 4.4.

2. The pseudo-second-order kinetic equation could be expressed as:

$$-dq_t/dt = k_2(q_e - q_t)^2 \quad \text{Eq. 4.5}$$

Separating the variable in equation (1) gives:

$$-d(q_e - q_t)/(q_e - q_t)^2 = k_2 \cdot dt \quad \text{Eq. 4.6}$$

Integrating both sides for the boundary condition $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = t$ gives the integrated rate law for a pseudo-second order reaction,

$$1/(q_e - q_t) = 1/q_e + k_2 \cdot t \quad \text{Eq. 4.7}$$

Equation (4.7) can be rearranged to obtain:

$$t/q_t = (1/k_2 \cdot q_e^2) + t/q_e \quad \text{Eq.4.8}$$

where:

k_2	pseudo second order kinetic constant rate (L/(mg.hr))
q_e	the adsorbed amount per adsorbent at equilibrium stage (mg/g)
q_t	the adsorbed amount per adsorbent at time (mg/g)
t	contact time (hr)

The kinetic constant, k_2 was calculated from intercept value $(1/k_2 \cdot q_e^2)$ of plotting between t/q_t against t using Eq. 4.8.

The kinetic experimental data of arsenate (As(V)) adsorption on four types of adsorbent were simulated by pseudo-first-order and pseudo-second-order rate equation (4.4) & (4.8). The results are listed in *Table 4.3* & *Table 4.4*.

Table 4.3 Pseudo-first-order kinetic parameters for arsenate (As(V)) adsorption by virgin activated carbon and iron oxide coated activated carbon

Adsorbent	$y = ax + b$	$q_e (exp)$ (mg/g)	Pseudo first order		
			R^2	k_1 (h^{-1})	$q_e (cal)$ (mg/g)
Fe-PAC	$y = -0.1558x - 1.7281$	0.226	0.95	0.156	0.018
Fe-GAC	$y = -0.1062x - 0.9099$	0.219	0.96	0.106	0.123
Virgin PAC	$y = -0.0074x - 0.8417$	0.215	0.74	0.007	0.143
Virgin GAC	$y = -0.1108x - 1.1363$	0.095	0.99	0.111	0.073

Table 4.4 Pseudo-second-order kinetic parameters for arsenate (As(V)) adsorption by virgin activated carbon and iron oxide coated activated carbon

Adsorbent	$y = ax + b$	$q_e (exp)$ (mg/g)	Pseudo second order		
			R^2	k_2 (g/mg-h)	$q_e (cal)$ (mg/g)
Fe-PAC	$y = 4.4779x + 0.1314$	0.226	0.99	152.6	0.223
Fe-GAC	$y = 4.5558x + 3.1084$	0.219	0.99	6.7	0.219
Virgin PAC	$y = 9.0005x + 5.9405$	0.215	0.99	13.6	0.111
Virgin GAC	$y = 10.201x + 12.869$	0.095	0.99	8.1	0.098

The results indicated that the experimental results are better described by pseudo-second-order model based on the R-square values. It was indicated that arsenate adsorption onto virgin activated carbons and iron oxide coated activated carbons may be chemisorption or chemical sorption involving valency forces through sharing of electron between adsorbent and adsorbate (Ho and McKay, 2000).

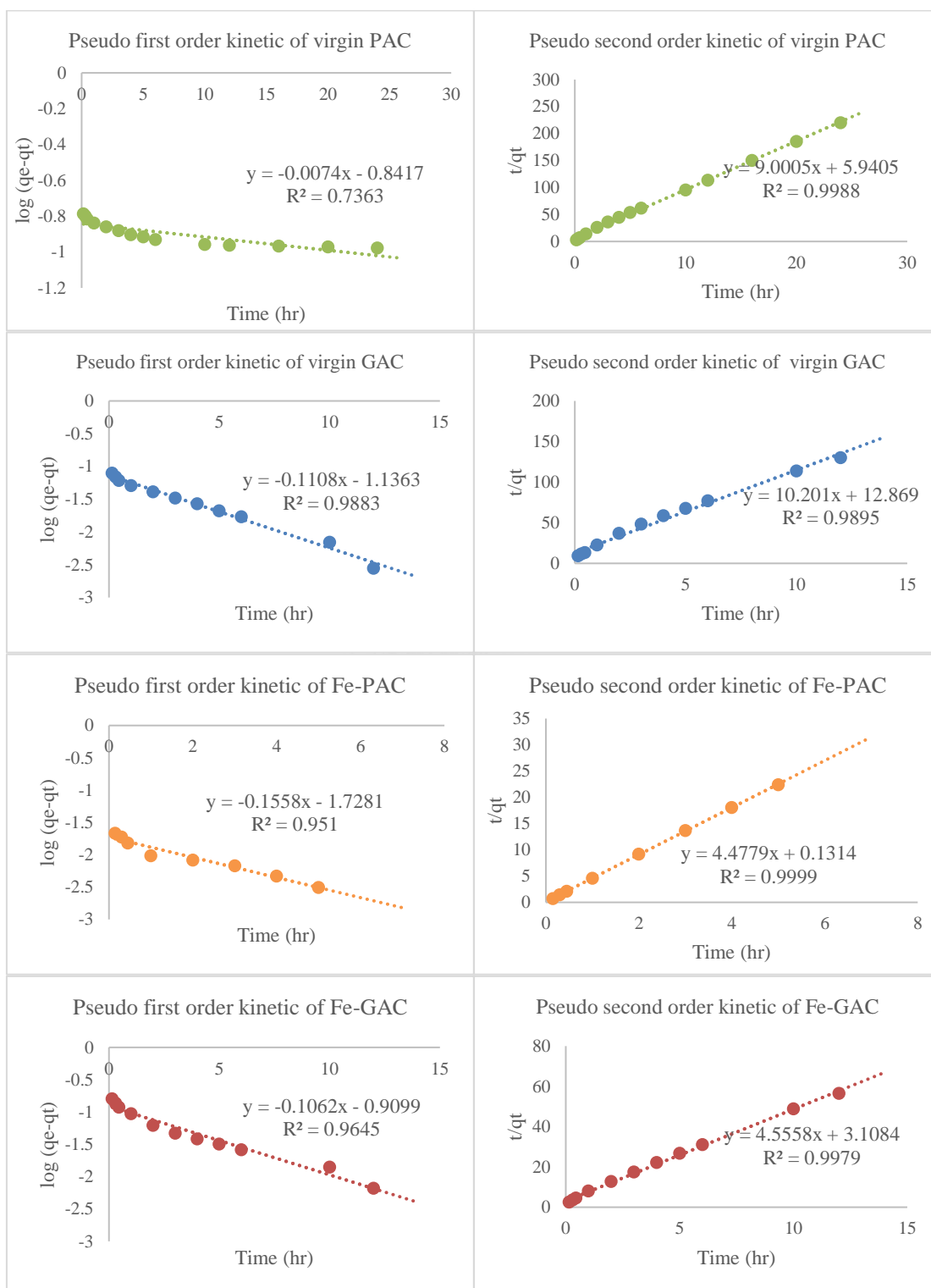


Figure 4.8 Adsorption kinetic of virgin activated carbons and iron oxide coated activated carbons by pseudo-first order and pseudo-second-order kinetic

4.2.4 Adsorbent dosage

The effect of adsorbent dosage on arsenate (As(V)) adsorption is shown in *Figure 4.9*, under experiment condition: the initial arsenate (As(V)) concentration of 1 mg/L, solution pH 5.0, adsorption time 16 hours and varied adsorbent dosage from 1.0 g/L to 6.0 g/L. The arsenate (As(V)) adsorption efficiency considerably increased with increasing adsorbent dosage. The increasing adsorbent dosage from 1.0 g/L to 5.0 g/L of four types of adsorbent result in an increase from 9.55% to 43.64%, 6.36% to 40.91%, 63.27% to 97.38% and 40.73% to 92.73% for virgin PAC, virgin GAC, Fe-PAC and Fe-GAC, respectively. It is proved that the increased adsorbent dosage can raise the arsenate removal percentage, due to the increased surface area of adsorbents available for arsenate (As(V)) adsorption (*Bazrafshan et al., 2013; Kord Mostafapour et al., 2012; Pandey et al., 2009*). The additional increase of adsorbent dose (>5.0 g/L) did not cause remarkable enhancement for arsenate (As(V)) adsorption. Hence, 5 g/L of virgin powdered activated carbon, virgin granular activated carbon, iron oxide coated powdered activated carbon and iron oxide coated granular activated were selected for other experiments.

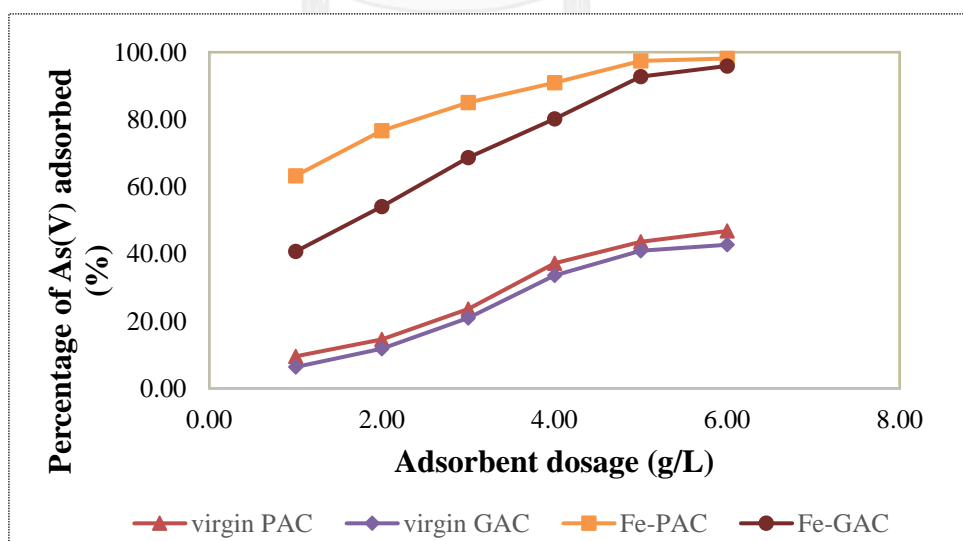
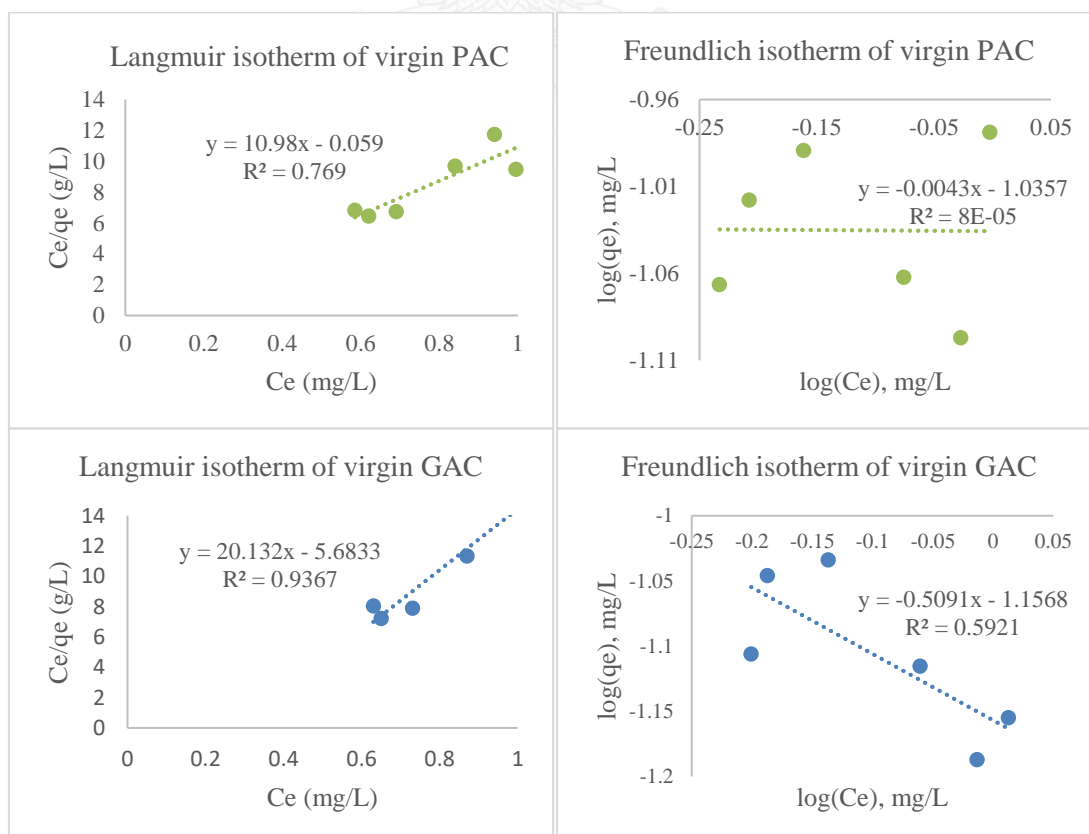


Figure 4.9 The effect of adsorbent dosage on arsenate (As(V)) adsorption

4.2.5 Adsorption isotherms on arsenate (As(V)) adsorption by virgin activated carbons and iron oxide coated activated carbons

The adsorption isotherm of arsenate (As(V)) adsorption indicates how the adsorption molecule distribute between the solid and liquid phase when the adsorption reaches the equilibrium state. The most widely used to describe the experimental data of the adsorption isotherm are Langmuir and Freundlich isotherm models. The adsorption isotherm of virgin activated carbons and iron oxide coated activated carbons were shown in *Figure 4.10*. These isotherms represent the adsorption behavior of arsenate (As(V)) on the different types of adsorbents in term of adsorbent dosage for a contact time 16 hours. All the isotherms were shown the increasing of adsorption capacity with increasing adsorbent dosage.

The result of arsenate (As(V)) adsorption on all adsorbents (*Figure 4.9*) were analyzed by using the Langmuir and Freundlich models to evaluate parameters associated to the adsorption behavior.



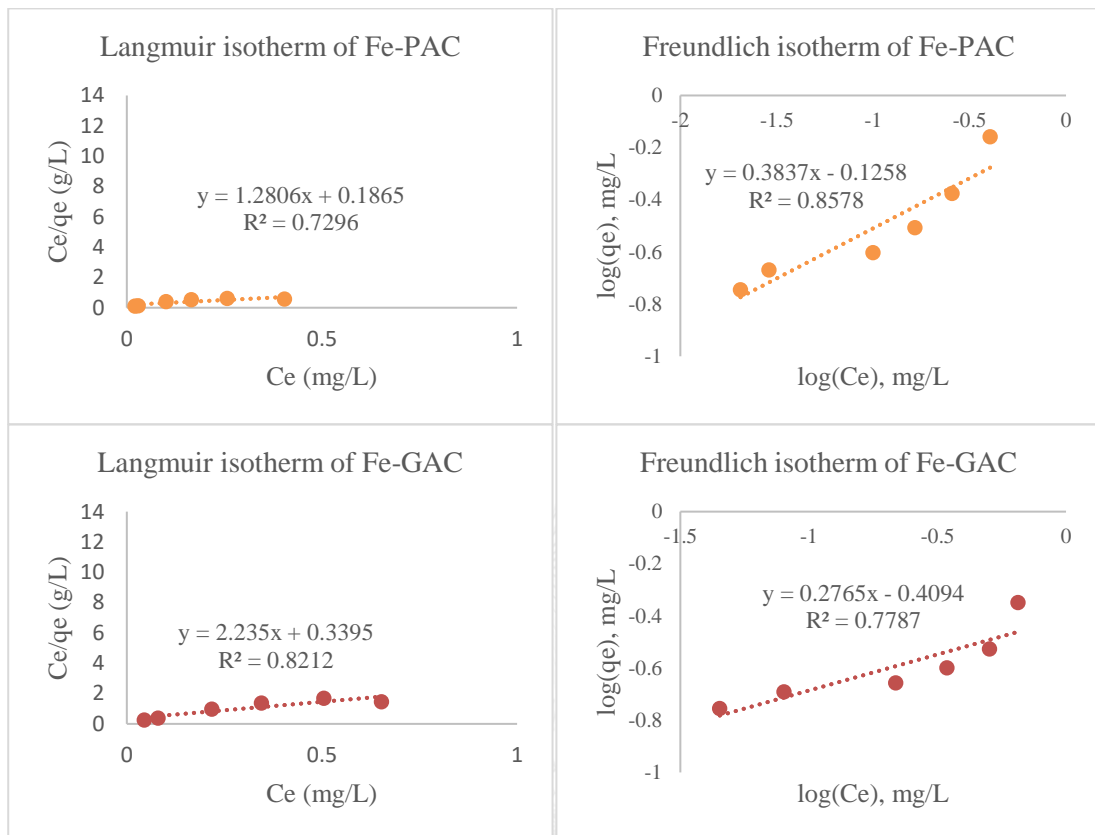


Figure 4.10 Adsorption isotherm of arsenate (As(V)) onto virgin coated activated carbon and iron oxide coated activated carbon

1. Langmuir isotherm model

All adsorptive sites are considered equivalent and there is no interaction between adsorbed molecules and adsorptive sites

The linear form of Langmuir equation at a given temperature is represented by:

$$q_e = q_m \cdot b \cdot c_e / (1 + b \cdot c_e) \quad \text{Eq. 4.9}$$

Equation 4.9 can be derived to obtain:

$$c_e/q_e = 1/(b \cdot q_m) + c_e/q_m \quad \text{Eq. 4.10}$$

where:

- q_m the maximum adsorption capacity (mg/g)
- c_e the equilibrium concentration of ion in liquid form (mg/L)
- q_e the arsenate amount adsorbs onto 1 g of adsorbent (mg/g)
- b the adsorption constant related to the energy of adsorption (L/mg)

2. Freundlich isotherm model

Freundlich model is multi-adsorptive site isotherm model for heterogeneous adsorptive surfaces.

The Freundlich model can be indicated by the following equation:

$$q_e = k_f \cdot c_e^{1/n} \quad \text{Eq. 4.11}$$

The equation is conveniently used in the linear form by taking the logarithm of both sides as:

$$\text{Log } q_e = \log K_f + (1/n) \log C_e \quad \text{Eq. 4.12}$$

where:

- c_e the equilibrium concentration of ion in liquid form (mg/L)
- q_e the arsenate amount adsorbs onto 1 g of adsorbent (mg/g)
- k_f, n the indicative isotherm parameters of adsorption capacity and intensity

Experimental isotherm data acquired were correlated with the linear form of Langmuir model, indicated that it is a monolayer adsorption. The isotherm parameters were listed in *Table 4.5* & *Table 4.6*. It could be seen that q_m , B and k_f are higher for arsenate (As(V)) adsorption onto iron oxide coated activated carbons than virgin activated carbons. Therefore, iron oxide coated activated carbons performed well in arsenate (As(V)) adsorption.

Table 4.5 The parameters of Langmuir equation

Adsorbent	Equation	Langmuir equation		
		q_m (mg/g)	B (L/mg)	R^2
Virgin PAC	$Y = 10.98x - 0.059$	0.091	-186.05	0.77
Virgin GAC	$Y = 20.132x - 5.6833$	0.050	-3.52	0.94
Fe-PAC	$Y = 1.2806x + 0.1865$	0.781	6.87	0.73
Fe-GAC	$Y = 2.2891x + 0.3137$	0.448	6.57	0.82

Table 4.6 The parameters of Freundlich equation

Adsorbent	Equation	Freundlich equation		
		$1/n$ (L/g)	k_f (mg/g)	R^2
Virgin PAC	$Y = -0.0043x - 1.0357$	-0.0043	0.09	0.05
Virgin GAC	$Y = -0.5091x - 1.1568$	-0.5091	0.07	0.56
Fe-PAC	$Y = 0.3837x - 0.1258$	0.3837	0.75	0.86
Fe-GAC	$Y = 0.2765x - 0.4094$	0.2765	0.39	0.78

4.2.6 The effect of ionic strength on arsenate (As(V)) adsorption

The effect of ionic strength on arsenate (As(V)) adsorption on four types of adsorbent were examined at different initial ionic strength from 0.00 M, 0.01 M and 0.1 M. Adsorption efficiency of arsenate (As(V)) was shown in *Figure 4.11*. Based on the adsorption data in *Figure 4.11*, arsenate adsorption percentage was increased at 0.01 M for all types of adsorbent. However, it didn't cause much change in arsenate (As(V)) adsorption.

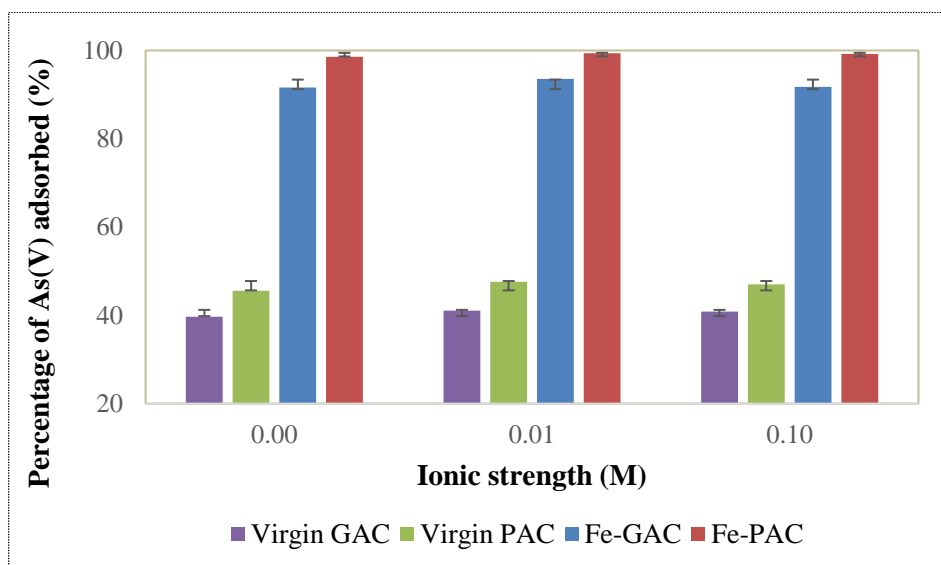


Figure 4.11 The effect of ionic strength on arsenate (As(V)) adsorption ($n=3$)

4.2.7 The effect of coexisting ions on arsenate (As(V)) adsorption

Numerous anionic components might exist in groundwater and might compete with arsenic for adsorption sites (Yao *et al.*, 2014). Among the major coexisting anionic components, iron is usually existing in groundwater perhaps inhibiting of arsenic removal. To examine the effect of co-existing ions on the arsenate (As(V)) adsorption, arsenate (As(V)) solution was mixed with 5.0 mg FeSO₄/L (3.16 mg/L as SO₄²⁻) and the arsenate adsorption was determined. Under the experiment conditions, the effect of coexisting ion on arsenate adsorption showed in Figure 4.12 that ferrous sulphate (FeSO₄) caused a lot of reduction in arsenate (As(V)) adsorption, due to the competition of the ions with arsenate (As(V)) on adsorbent pores. The coexisting ion was decreased the adsorption of arsenate from 43.64 to 29.9, 40.91 to 23.4, 97.38 to 76.7 and 92.73 to 70.4 for virgin PAC, virgin GAC, Fe-PAC and Fe-GAC, respectively.

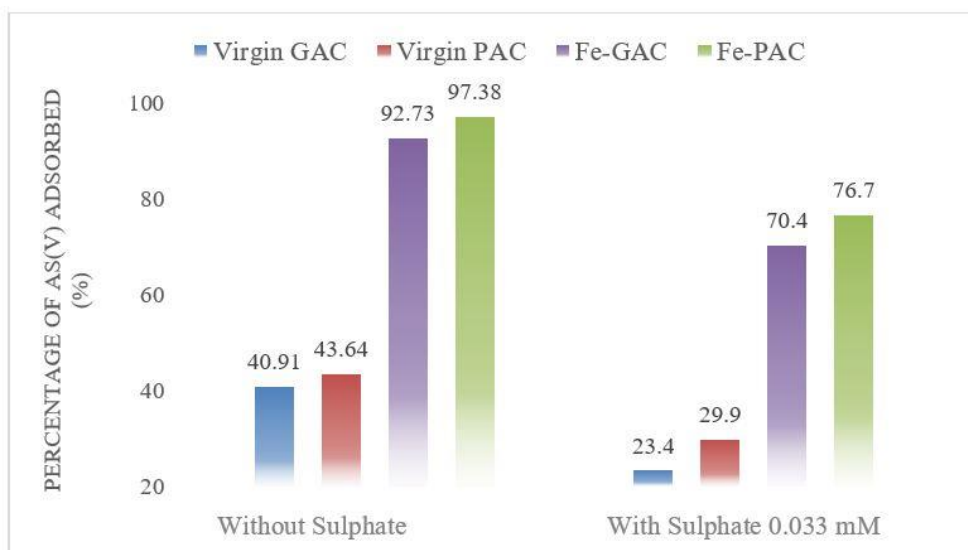


Figure 4.12 The effect of coexisting ion on arsenate (As(V)) adsorption

4.3 Rapid Lab-scale Column Test on arsenate (As(V)) adsorption

Based on the batch experiment results, iron oxide coated powdered activated carbon is the best adsorbent on arsenate (As(V)) adsorption followed by iron oxide coated granular activated carbon. However, iron oxide granular activated carbon was chosen as the adsorbent used in the arsenate (As(V)) adsorption in column test. Figure 4.13 represents the schematic diagram of the rapid lab scale column system.

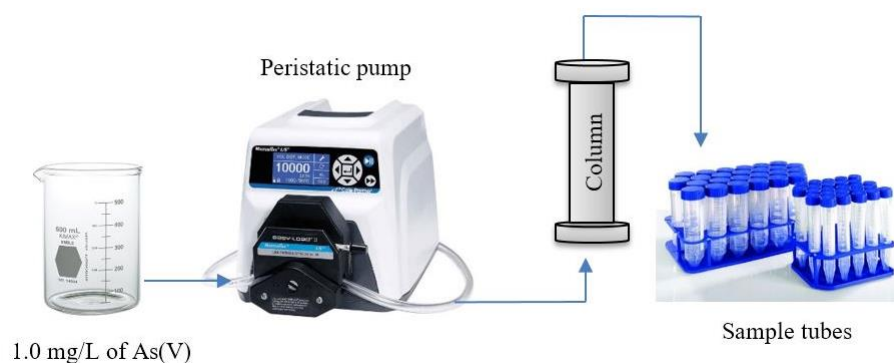


Figure 4.13 The schematic diagram of the rapid lab-scale column system.

4.3.1 The arsenate (As(V)) adsorption efficiency onto iron oxide coated granular activated carbon

Figure 4.14 presented the breakthrough curve of arsenate(As(V)) adsorption onto the iron oxide coated granular activated carbon using 5.0 g of adsorbent and 1.0 ml/min. As it shows, a breakthrough point was reached at 120 hours after running the column test. The low initial concentration of arsenate (As(V)) contributed to an extended breakthrough curve, demonstrating that a higher volume of arsenate solution could be treated.

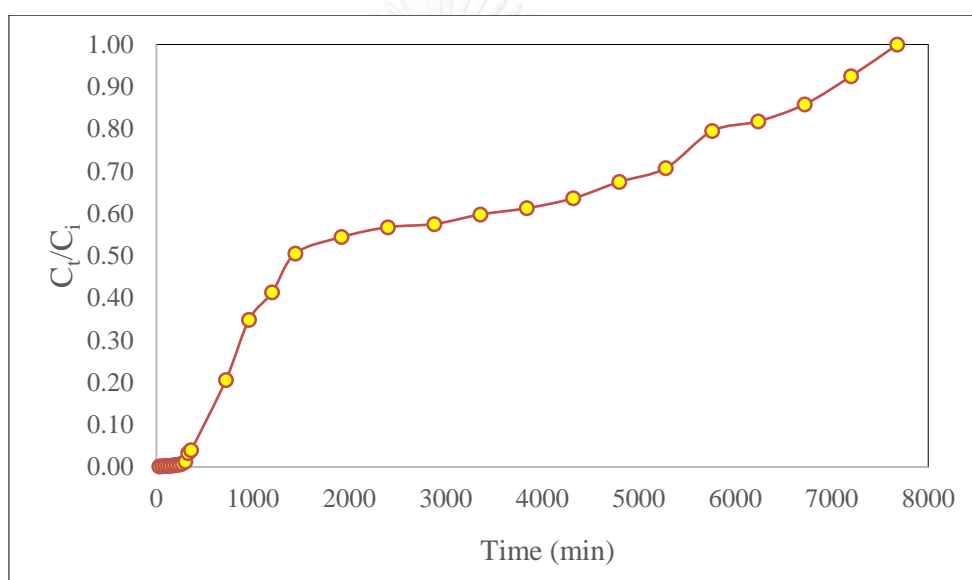


Figure 4.14 Breakthrough curve for arsenate (As(V)) adsorption on iron oxide coated granular activated carbon

4.3.2 Modelling of analytical result on arsenate (As(V)) adsorption onto iron oxide coated granular activated carbon

The dynamic behavior of the column was predicted using Thomas models, which is used to present the performance of the column (Thomas 1994). This mentioned model was assumed that the adsorption characteristic follows Langmuir isotherm while second-order is the reaction kinetics of driving forces. The theoretical form of the model is given as:

$$\ln \left(\frac{C_0}{C_t} - 1 \right) = \frac{K_{Th} q_0 m}{Q} - \frac{K_{Th} C_0}{Q} (V_{eff}) \quad \text{Eq. 5.1}$$

where:

K_{Th} Constant rate of Thomas model ($\text{mL} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$)

q_0 The equilibrium adsorbate uptake (mg/g)

m The adsorbent amount in the column (g)

V_{eff} The volume of the solution (L)

Q The flowrate (mL/min)

The column breakthrough curve for iron oxide coated granular activated carbon, with flow rate 1 mL/min, shows fast uptake of arsenate in the first stage and rapid decrease in the second stage, it might due to saturation was reached and significant increase to breakthrough point in third stage. Due to the three stage occurs in breakthrough curve, the data for the adsorption column was divided into three graphs.

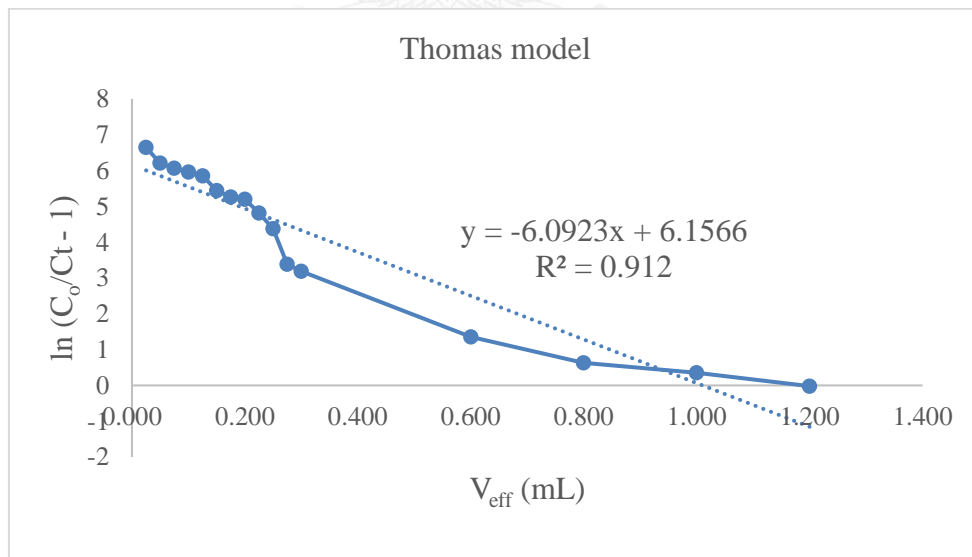


Figure 4.15 Thomas Modelling of analytical result on arsenate (As(V)) adsorption onto iron oxide coated granular activated carbon (1st stage)

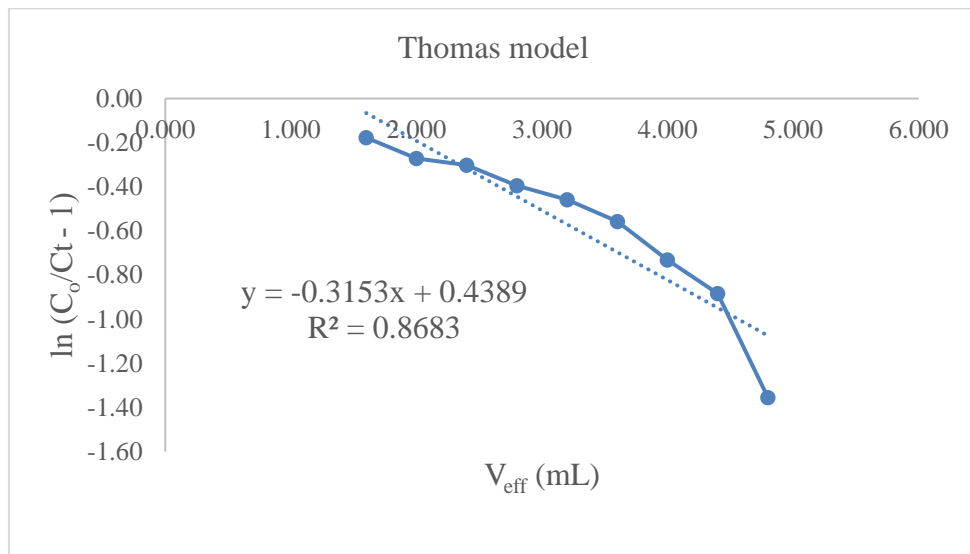


Figure 4.16 Thomas Modelling of analytical result on arsenate (As(V)) adsorption onto iron oxide coated granular activated carbon (2nd stage)

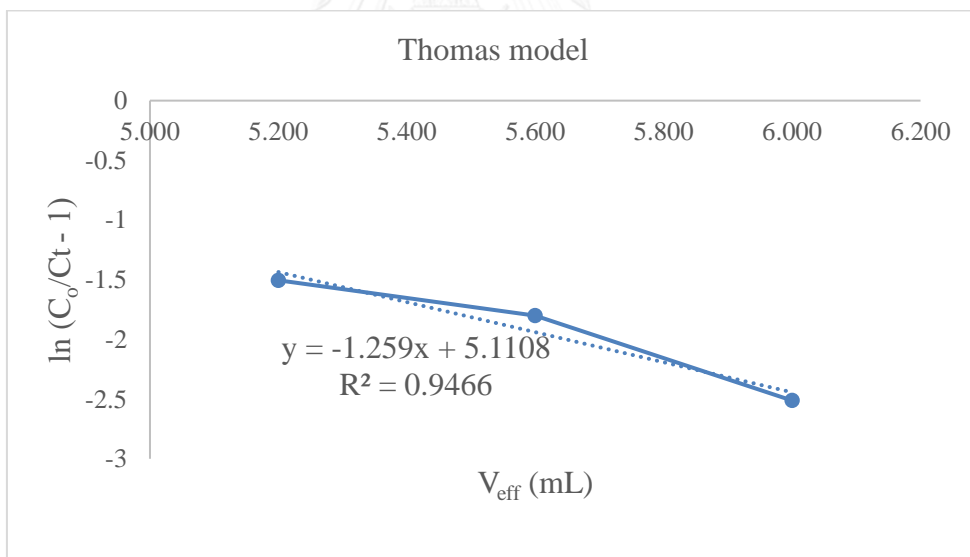


Figure 4.17 Thomas Modelling of analytical result on arsenate (As(V)) adsorption onto iron oxide coated granular activated carbon (3rd stage)

Table 4.7 Thomas model parameters for arsenate (As(V)) adsorption

Initial concentration of arsenate (As(V))	1 st stage	2 nd stage	3 rd stage
$K_{Th} (mL.mg^{-1}.min^{-1})$	5.07	0.2	1.05
$q_o (mg/g)$	0.24	0.24	0.97
R^2	0.91	0.95	0.94

4.3.3 The regeneration of iron oxide coated granular activated carbon

After regeneration, the adsorbents were washed with de-ionized water (18 MΩ) through column for 45 minutes until rinsing water became neutral (pH 7 ± 0.2). Figure 4.18 & Figure 4.19 shown the arsenate (As(V)) adsorption after regeneration of iron oxide coated granular activated carbon.

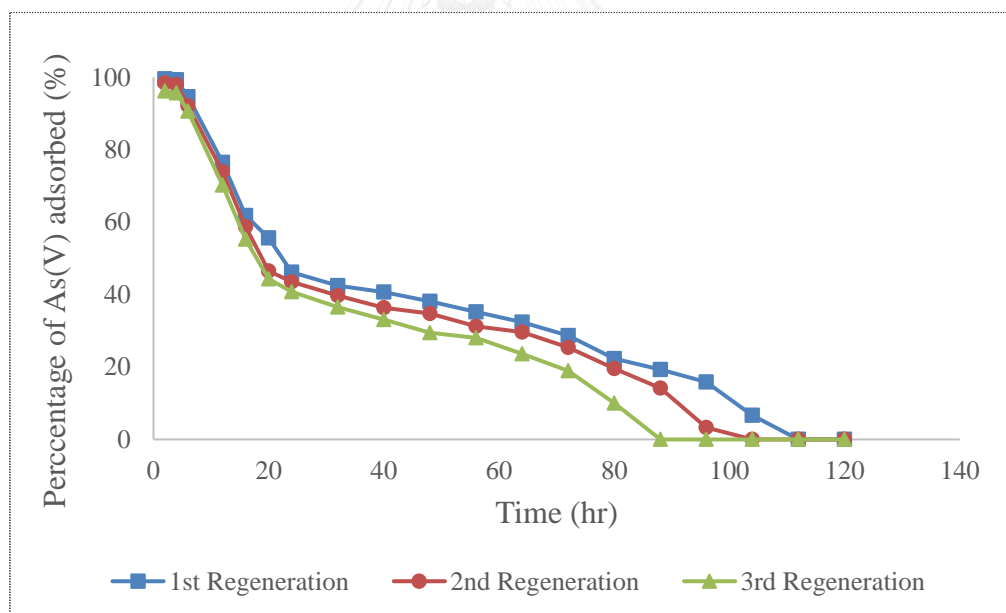


Figure 4.18 The arsenate (As(V)) adsorption after regeneration

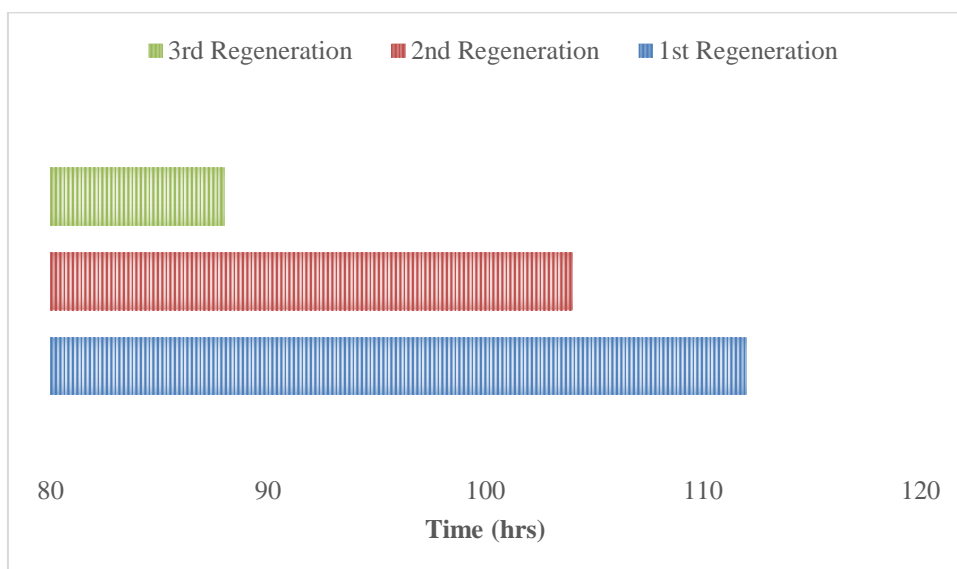


Figure 4.19 Effect of regeneration on Arsenate (As(V)) adsorption

Figure 4.18 & Figure 4.19 show the arsenate (As(V)) adsorption after regeneration of iron oxide coated granular activated carbon. It was found that the breakthrough points ($C/C_0 = 1.0$) of 1st, 2nd and 3rd time of regeneration were 112, 104 and 88 hours, respectively; which decrease from 120 hours before regeneration. It was proved that arsenate (As(V)) adsorption percentages decreased with increasing the regeneration cycle due to arsenate was attracted by iron oxide. When doing the regeneration, iron oxide on the surface area of adsorbent was fallen off (*Hu et al., 2015*).

4.4 Cost analysis

From the experiment results, iron oxide coated powdered/granular activated carbons can adsorb arsenate (As(V)) more than virgin powdered/granular activated carbon more than 50%. Although, iron oxide coated activated carbon (five time coated) cost 5 times more expensive than virgin activated carbon but the efficiency of this adsorbent was accepted in the arsenate adsorption and after the regeneration of iron oxide coated granular activated carbon, the adsorption efficiency is still higher than virgin activated carbon. Therefore, if comparing the price and its efficiency, iron

oxide coated activated carbon would be recommended to an effective adsorbent for the next study. The cost analysis was shown in *Table 4.8*.

Table 4.8 The cost analysis of the adsorbent

Adsorbent	Adsorbent and chemical costs	Average treatment cost		Removal efficiency
	per 100g	per liter	per m ³	
Activated carbon (FILTRASORB 200)	\$ 4.29	\$ 0.64	\$ 643	41%
Iron oxide coated activated carbon (FILTRASORB 200)	\$ 21.86	\$ 1.1	\$ 1093	93%



CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The objective of this research was to characterize the surface structure of the adsorbents, in terms of specific surface area and pore size distribution, the influencing factors, i.e. solution pH, contact time, adsorbent dosage, ionic strength and co-existing ions, on the arsenate adsorption onto virgin and iron oxide coating activated carbons in arsenate synthetic groundwater by batch adsorption experiment, and to compare the arsenate adsorption efficiency and evaluate the treatment cost among four adsorbents tested. The results of this research can be concluded as the following:

5.1.1 Characterization of adsorbent

The adsorbents were characterized by using SEM-EDX and specific surface area analyzer. From the characterization results, it was found that surface area and total pore volume of virgin powdered activated carbon and virgin granular activated carbon were decreased after being coated with iron oxide, which decreased from 768.06 to 561.38 and 765.86 to 721.89, respectively. Fe percentages were increased after coating with iron oxide from 0.15% to 3.73% for Fe-PAC and 0.58% to 4.21% for Fe-GAC. It indicated that iron oxide was impregnated onto powdered/granular activated carbon.

5.1.2 Batch adsorption experiment

- From the batch experiment to determine the optimal solution pH for the arsenic elimination with 4 types of adsorbents, it is found that virgin granular activated carbon, virgin powdered activated carbon, iron oxide coated granular activated carbon and iron oxide coated powdered activated carbon provided maximum removal efficiency at the solution pH of 4 that offer the arsenic removal percentage of 42.67%, 46%, 97.50% and 97.43%, respectively. The solution pH of 5 (*please refer to*

Appendix 1), which was similar to the real arsenic containing groundwater in Laos, was set to prepare the arsenate synthetic groundwater.

- From the experiment to determine the optimal contact time to reach the adsorption equilibrium in the arsenic elimination with 4 types of adsorbents, it is found that 16 hours provided the best removal percentages of 40.25, 45.08%, 92.80% and 97.36% for all of adsorbents: virgin granular activated carbon, virgin powdered activated carbon, iron oxide coated granular activated carbon and iron oxide coated powdered activated carbon, respectively.

- From the experiment to determine the optimal adsorbent dosage for the arsenic elimination with 4 types of adsorbent, it is found that all of adsorbents provided the best adsorption at 5.0 g of adsorbent per liter. Based on the adsorption analysis results with 4 types of adsorbent, the adsorption isotherm data obeyed Langmuir adsorption isotherm, which suggests that the arsenate adsorption by the activated carbons was mono-layer adsorption.

- From the experiment to determine the optimal ionic strength for the arsenic removal with 4 types of adsorbents, found that virgin granular activated carbon, virgin powdered activated carbon, iron oxide coated granular activated carbon and iron oxide coated powdered activated carbon exhibited the best adsorption capacity at 0.01 M, with the arsenic removal percentage of 41.0%, 47.6%, 93.6% and 99.3%, respectively.

- From the experiment to determine the effect of co-existing ion such as ferrous sulfate in arsenic eliminating with 4 types of adsorbents: virgin granular activated carbon, virgin powdered activated carbon, iron oxide coated granular activated carbon and iron oxide coated powdered activated carbon, it is found that ferrous sulfate affected the arsenic adsorption because ferrous sulfate was adsorbed to pore site of activated carbon, which had decreased arsenic removal percentage from 43.64 to 29.9, 40.91 to 23.4, 97.38 to 76.7 and 92.73 to 70.4 for virgin PAC, virgin GAC, Fe-PAC and Fe-GAC, respectively.

- From all the batch adsorption experiment, the adsorbent that give the highest efficiency in eliminating arsenate is the iron oxide coated powder activated

carbon, followed by the iron oxide coated granular activated carbon, virgin powdered activated carbon and virgin granular activated carbon, respectively.

5.1.3 Column adsorption experiment

The adsorption efficiency of arsenate, iron oxide coated granular activated carbon was put into a column due to it has the best adsorption efficiency and ease to regenerate. From the column experiment, the breakthrough point is at 112 hours.

5.1.4 Regeneration experiment

From the regeneration experiment with iron oxide coated granular activated carbon for reuse, when compare with 3 times of regeneration found that the breakthrough came earlier from 120 hours for virgin activated carbon to 112, 104 and 88 hours, for 1st, 2nd and 3rd regeneration, respectively.

5.2 Recommendation

Based on the experiment result of this research, several recommendations for future research was proposed as follows:

- For the adsorbent development, the mixing of activated carbon with other materials or chemical should be studied and tested to confirm the ability of adsorbent.
- For the influencing factors of the arsenic adsorption, the presence of various heavy metals such as zinc (Zn^{2+}), cadmium (Cd^{2+}), copper (Cu^{2+}), lead (Pb^{2+}), etc.
- For well understanding the column experiment, the column should be scaled up for apply in the household with the real groundwater containing arsenic.
- For the exhausted adsorbent, it should be considered about hazardous waste management and further research to treat arsenate-activated carbon waste is required.

REFERENCES

- Aksu, Z., and Gönen, F. (2004). Biosorption of phenol by immobilized activated sludge in a continuous packed bed: prediction of breakthrough curves. *Process biochemistry*, 39(5), 599-613.
- Al-Degs, Y. S., El-Barghouthi, M. I., El-Sheikh, A. H., and Walker, G. M. (2008). Effect of solution pH, ionic strength, and temperature on adsorption behavior of reactive dyes on activated carbon. *Dyes and pigments*, 77(1), 16-23.
- Ali, I. (2012). New generation adsorbents for water treatment. *Chemical Reviews*, 112(10), 5073-5091.
- Asadullah, M., Jahan, I., Ahmed, M. B., Adawiyah, P., Malek, N. H., and Rahman, M. S. (2014). Preparation of microporous activated carbon and its modification for arsenic removal from water. *Journal of Industrial and Engineering Chemistry*, 20(3), 887-896.
- Bajpai, S., and Chaudhuri, M. (1999). Removal of arsenic from ground water by manganese dioxide-coated sand. *Journal of Environmental Engineering*, 125(8), 782-784.
- Bazrafshan, E., Faridi, H., Mostafapour, F. K., and Mahvi, A. H. (2013). Removal of arsenic from aqueous environments using Moringa Peregrina seed extract as a natural coagulant. *Asian Journal of Chemistry*, 25(7), 3557.
- Bielicka-Daszkiewicz, K., and Voelkel, A. (2009). Theoretical and experimental methods of determination of the breakthrough volume of SPE sorbents. *Talanta*, 80(2), 614-621.
- Budinova, T., Savova, D., Tsyntsarski, B., Ania, C. O., Cabal, B., Parra, J. B., et al. (2009). Biomass waste-derived activated carbon for the removal of arsenic and manganese ions from aqueous solutions. *Applied Surface Science*, 255(8), 4650-4657.
- Chammui, Y., Sooksamiti, P., Naksata, W., Thiansem, S., and Arqueropanyo, O.-a. (2014). Removal of arsenic from aqueous solution by adsorption on Leonardite. *Chemical Engineering Journal*, 240, 202-210.
- Chang, Q., Lin, W., and Ying, W.-c. (2010). Preparation of iron-impregnated granular activated carbon for arsenic removal from drinking water. *Journal of hazardous materials*, 184(1), 515-522.
- Chen, W., Parette, R., Zou, J., Cannon, F. S., and Dempsey, B. A. (2007). Arsenic removal by iron-modified activated carbon. *Water research*, 41(9), 1851-1858.
- Chowdhury, Z., Zain, S., Rashid, A., Rafique, R., and Khalid, K. (2012). Breakthrough curve analysis for column dynamics sorption of Mn (II) ions from wastewater by using Mangostana garcinia peel-based granular-activated carbon. *Journal of Chemistry*, 2013.

- Chu, K. (2004). Improved fixed bed models for metal biosorption. *Chemical Engineering Journal*, 97(2), 233-239.
- Crittenden, J. C., Trussell, R. R., Hand, D. W., Howe, K. J., and Tchobanoglous, G. (2012). *MWH's water treatment: principles and design*: John Wiley & Sons.
- Diamadopoulos, E., Ioannidis, S., and Sakellaropoulos, G. P. (1993). As (V) removal from aqueous solutions by fly ash. *Water research*, 27(12), 1773-1777.
- Faust, S. D., and Aly, O. M. (2013). *Adsorption processes for water treatment*.
- Fierro, V., Muniz, G., Gonzalez-Sánchez, G., Ballinas, M., and Celzard, A. (2009). Arsenic removal by iron-doped activated carbons prepared by ferric chloride forced hydrolysis. *Journal of hazardous materials*, 168(1), 430-437.
- Gu, Z., Fang, J., and Deng, B. (2005). Preparation and evaluation of GAC-based iron-containing adsorbents for arsenic removal. *Environmental science & technology*, 39(10), 3833-3843.
- Gulnaz, O., Sahmurova, A., and Kama, S. (2011). Removal of Reactive Red 198 from aqueous solution by *Potamogeton crispus*. *Chemical Engineering Journal*, 174(2), 579-585.
- Gupta, V., Saini, V., and Jain, N. (2005). Adsorption of As (III) from aqueous solutions by iron oxide-coated sand. *Journal of colloid and Interface Science*, 288(1), 55-60.
- Ho, Y.-S., and McKay, G. (2000). The kinetics of sorption of divalent metal ions onto sphagnum moss peat. *Water research*, 34(3), 735-742.
- Höll, W. H. (2010). Mechanisms of arsenic removal from water. *Environmental geochemistry and health*, 32(4), 287-290.
- Hu, X., Ding, Z., Zimmerman, A. R., Wang, S., and Gao, B. (2015). Batch and column sorption of arsenic onto iron-impregnated biochar synthesized through hydrolysis. *Water research*, 68, 206-216.
- Hughes, M. F. (2002). Arsenic toxicity and potential mechanisms of action. *Toxicology letters*, 133(1), 1-16.
- Jain, C., and Ali, I. (2000). Arsenic: occurrence, toxicity and speciation techniques. *Water research*, 34(17), 4304-4312.
- Jang, M., Chen, W., and Cannon, F. S. (2008). Preloading hydrous ferric oxide into granular activated carbon for arsenic removal. *Environmental science & technology*, 42(9), 3369-3374.
- Jang, M., Min, S.-H., Kim, T.-H., and Park, J. K. (2006). Removal of arsenite and arsenate using hydrous ferric oxide incorporated into naturally occurring porous diatomite. *Environmental science & technology*, 40(5), 1636-1643.
- Kamala, C., Chu, K., Chary, N., Pandey, P., Ramesh, S., Sastry, A., et al. (2005). Removal of arsenic (III) from aqueous solutions using fresh and immobilized plant biomass. *Water research*, 39(13), 2815-2826.

- Kapaj, S., Peterson, H., Liber, K., and Bhattacharya, P. (2006). Human health effects from chronic arsenic poisoning—a review. *Journal of Environmental Science and Health Part A*, 41(10), 2399-2428.
- Kartinen, E. O., and Martin, C. J. (1995). An overview of arsenic removal processes. *Desalination*, 103(1), 79-88.
- Katsoyiannis, I. A., and Zouboulis, A. I. (2006). Use of Iron- and Manganese-Oxidizing Bacteria for the Combined Removal of Iron, Manganese and Arsenic from Contaminated Groundwater. *Water Quality Research Journal of Canada*, 41(2), 117-129.
- Kim, M.-J., Nriagu, J., and Haack, S. (2002). Arsenic species and chemistry in groundwater of southeast Michigan. *Environmental Pollution*, 120(2), 379-390.
- Kord Mostafapour, F., Bazrafshan, E., Farzadkia, M., and Amini, S. (2012). Arsenic removal from aqueous solutions by *Salvadora Persica* stem ash. *Journal of Chemistry*, 2013.
- Kundu, S., and Gupta, A. (2005). Analysis and modeling of fixed bed column operations on As (V) removal by adsorption onto iron oxide-coated cement (IOCC). *Journal of colloid and Interface Science*, 290(1), 52-60.
- Lata, S., Singh, P., and Samadder, S. (2015). Regeneration of adsorbents and recovery of heavy metals: a review. *International Journal of Environmental Science and Technology*, 12(4), 1461-1478.
- Lin, T.-F., and Wu, J.-K. (2001). Adsorption of arsenite and arsenate within activated alumina grains: equilibrium and kinetics. *Water research*, 35(8), 2049-2057.
- Liu, Z., Zhang, F.-S., and Sasai, R. (2010). Arsenate removal from water using Fe³⁺O₄-loaded activated carbon prepared from waste biomass. *Chemical Engineering Journal*, 160(1), 57-62.
- Mattson, J. S., and Mark, H. B. (1971). *Activated Carbon: Surface Chemistry and Adsorption from Solution*: M. Dekker.
- Meharg, A. A., and Hartley-Whitaker, J. (2002). Arsenic uptake and metabolism in arsenic resistant and nonresistant plant species. *New Phytologist*, 154(1), 29-43.
- Mohan, D., and Pittman, C. U. (2007). Arsenic removal from water/wastewater using adsorbents—a critical review. *Journal of hazardous materials*, 142(1), 1-53.
- Mondal, P., Balomajumder, C., and Mohanty, B. (2007). A laboratory study for the treatment of arsenic, iron, and manganese bearing ground water using Fe³⁺ impregnated activated carbon: effects of shaking time, pH and temperature. *Journal of hazardous materials*, 144(1), 420-426.
- Mondal, P., Majumder, C., and Mohanty, B. (2008). Effects of adsorbent dose, its particle size and initial arsenic concentration on the removal of arsenic, iron and manganese from simulated ground water by Fe³⁺ impregnated activated carbon. *Journal of hazardous materials*, 150(3), 695-702.

- Naja, G., and Volesky, B. (2006). Behavior of the mass transfer zone in a biosorption column. *Environmental science & technology*, 40(12), 3996-4003.
- Oliveira, L. C., Rios, R. V., Fabris, J. D., Garg, V., Sapag, K., and Lago, R. M. (2002). Activated carbon/iron oxide magnetic composites for the adsorption of contaminants in water. *Carbon*, 40(12), 2177-2183.
- Pandey, P. K., Choubey, S., Verma, Y., Pandey, M., and Chandrashekhar, K. (2009). Biosorptive removal of arsenic from drinking water. *Bioresource technology*, 100(2), 634-637.
- Pattanayak, J., Mondal, K., Mathew, S., and Lalvani, S. (2000). A parametric evaluation of the removal of As (V) and As (III) by carbon-based adsorbents. *Carbon*, 38(4), 589-596.
- Saad, D. M., Cukrowska, E., and Tutu, H. (2015). Column adsorption studies for the removal of U by phosphonated cross-linked polyethylenimine: modelling and optimization. *Applied Water Science*, 5(1), 57-63. doi:10.1007/s13201-014-0162-1
- Selene, C.-H., Chou, J., and De Rosa, C. T. (2003). Case studies—arsenic. *International journal of hygiene and environmental health*, 206(4-5), 381-386.
- Smedley, P., and Kinniburgh, D. (2002). A review of the source, behaviour and distribution of arsenic in natural waters. *Applied geochemistry*, 17(5), 517-568.
- Sullivan, C., Tyrer, M., Cheeseman, C. R., and Graham, N. J. (2010). Disposal of water treatment wastes containing arsenic—a review. *Science of the Total Environment*, 408(8), 1770-1778.
- Sundstrom, D. W., and Klei, H. E. (1979). *Wastewater treatment*: Prentice Hall.
- Thirunavukkarasu, O., Viraraghavan, T., and Subramanian, K. (2003). Arsenic removal from drinking water using iron oxide-coated sand. *Water, Air, & Soil Pollution*, 142(1), 95-111.
- Thomas, H. C. (1944). Heterogeneous Ion Exchange in a Flowing System. *Journal of the American Chemical Society*, 66(10), 1664-1666. doi:10.1021/ja01238a017
- Tuna, A. Ö. A., Özdemir, E., Şimşek, E. B., and Beker, U. (2013). Removal of As (V) from aqueous solution by activated carbon-based hybrid adsorbents: Impact of experimental conditions. *Chemical Engineering Journal*, 223, 116-128.
- Viraraghavan, T., Subramanian, K., and Aruldoss, J. (1999). Arsenic in drinking water—problems and solutions. *Water Science and Technology*, 40(2), 69-76.
- Vitela-Rodriguez, A. V., and Rangel-Mendez, J. R. (2013). Arsenic removal by modified activated carbons with iron hydro (oxide) nanoparticles. *Journal of environmental management*, 114, 225-231.
- Wang, S., and Mulligan, C. N. (2006). Occurrence of arsenic contamination in Canada: sources, behavior and distribution. *Science of the Total Environment*, 366(2), 701-721.
- WHO. (2011). *Guidelines for Drinking-water Quality*. WHO chronicle, 38, 104-108.

- Worch, E. (2012). Adsorption technology in water treatment: fundamentals, processes, and modeling: Walter de Gruyter.
- Yao, S., Liu, Z., and Shi, Z. (2014). Arsenic removal from aqueous solutions by adsorption onto iron oxide/activated carbon magnetic composite. *Journal of Environmental Health Science and Engineering*, 12(1), 58.
- Zhang, Q. L., Lin, Y., Chen, X., and Gao, N. Y. (2007). A method for preparing ferric activated carbon composites adsorbents to remove arsenic from drinking water. *Journal of hazardous materials*, 148(3), 671-678.
- Zouboulis, A., Kydros, K., and Matis, K. (1993). Arsenic (III) and arsenic (V) removal from solutions by pyrite fines. *Separation science and technology*, 28(15-16), 2449-2463.



APPENDIX



จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

Appendix 1: Physicochemical parameter of groundwater in Champasak province
(Southern part of Laos)



Google earth image at Khetngong Village

Station	GPS		Depth (m)	pH	Arsenic concentration mg/L
DW1	N 14°46'20.8"	E 106°2'17.1"	27	5.60	0.967
DW2	N 14°46'19.5"	E 106°2'14.5"	27	6.30	0.732
DW3	N 14°46'14.8"	E 106°2'18.5"	24	4.86	0.291
DW4	N 14°46'14.8"	E 106°2'17.6"	21	7.01	0.470
DW5	N 14°46'15.4"	E 106°2'21.4"	27	6.03	0.370
DW6	N 14°46'15.2"	E 106°2'23.3"	23	6.18	0.285
DW7	N 14°46'15.0"	E 106°2'25.4"	24	5.49	0.556
DW8	N 14°46'11.8"	E 106°2'18.6"	27	6.15	0.815
DW9	N 14°46'10.0"	E 106°2'16.7"	27	5.49	0.438
DW10	N 14°46'9.5"	E 106°2'14.2"	24	6.56	0.565
DW11	N 14°46'8.6"	E 106°2'13.3"	27	5.27	0.323
DW12	N 14°46'11.3"	E 106°2'15.2"	21	5.12	0.743

Appendix 2-1: Effect of equilibrium solution pH on arsenate (As(V)) adsorption onto **Virgin powdered activated carbon** (experiment condition employed: Initial concentration 1.0 mg/L as AsO₄, adsorbent dosage 5 g/L, adsorption time 24 hours).

Mass (g/L)	pH _I	pH _F	Initial conc (mg/L)	Final concentration (mg/L)				%R As
				1	2	3	Avg ± SD	
5.0	2.01	2.05	0.967	0.635	0.638	0.639	0.637 ± 0.002	34.13
5.0	3.06	3.08	1.040	0.602	0.602	0.601	0.602 ± 0.006	42.12
5.0	4.03	4.05	1.050	0.569	0.568	0.563	0.567 ± 0.003	46.00
5.0	5.06	5.01	1.090	0.649	0.646	0.641	0.645 ± 0.004	40.83
5.0	6.04	6.2	1.150	0.798	0.799	0.798	0.798 ± 0.001	30.61
5.0	7.04	6.92	1.160	0.956	0.956	0.956	0.956 ± 0.000	17.59
5.0	8.04	7.8	1.000	0.953	0.951	0.952	0.952 ± 0.001	4.80
5.0	9.01	8.35	1.120	1.121	1.121	1.120	1.120 ± 0.000	0.00
5.0	10.02	9.44	1.100	1.099	1.100	1.100	1.100 ± 0.000	0.00

Appendix 2-2: Effect of equilibrium solution pH on arsenate (As(V)) adsorption onto **Virgin granular activated carbon** (experiment condition employed: Initial concentration 1.0 mg/L as AsO₄, adsorbent dosage 5 g/L, adsorption time 24 hours).

Mass (g/L)	pH _I	pH _F	Initial conc (mg/L)	Final concentration (mg/L)				%R As
				1	2	3	Avg ± SD	
5.0	2.01	2.08	0.967	0.678	0.679	0.678	0.678 ± 0.001	29.89
5.0	3.06	3.06	1.040	0.655	0.657	0.654	0.655 ± 0.002	37.02
5.0	4.03	4.07	1.050	0.599	0.604	0.602	0.602 ± 0.003	42.67
5.0	5.06	5.17	1.090	0.691	0.693	0.691	0.691 ± 0.001	36.61
5.0	6.04	6.05	1.150	0.859	0.858	0.851	0.856 ± 0.004	25.57
5.0	7.04	7.12	1.160	1.059	1.057	1.062	1.060 ± 0.003	8.62
5.0	8.04	8.07	1.000	0.975	0.979	0.980	0.978 ± 0.003	2.20
5.0	9.01	8.33	1.120	1.118	1.121	1.120	1.120 ± 0.003	0.00
5.0	10.02	9.56	1.100	1.097	1.100	1.102	1.100 ± 0.003	0.00

Appendix 2-3: Effect of equilibrium solution pH on arsenate (As(V)) adsorption onto **Iron oxide coated granular activated carbon** (experiment condition employed: Initial concentration 1.0 mg/L as AsO₄, adsorbent dosage 5 g/L, adsorption time 24 hours).

Mass (g/L)	pH _I	pH _F	Initial conc (mg/L)	Final concentration (mg/L)				%R As
				1	2	3	Avg ± SD	
5.0	2.01	2.03	0.967	0.042	0.041	0.040	0.041±0.001	95.76
5.0	3.06	3.08	1.040	0.032	0.032	0.032	0.032±0.000	96.92
5.0	4.03	4.05	1.050	0.009	0.011	0.009	0.010±0.001	99.05
5.0	5.06	5.09	1.090	0.061	0.059	0.060	0.060±0.001	94.50
5.0	6.04	5.97	1.150	0.651	0.649	0.651	0.650±0.001	43.48
5.0	7.04	6.87	1.160	0.922	0.919	0.920	0.920±0.002	20.69
5.0	8.04	7.55	1.000	0.851	0.850	0.850	0.850±0.001	15.00
5.0	9.01	8.65	1.120	0.973	0.971	0.972	0.972±0.001	13.21
5.0	10.02	9.76	1.100	0.963	0.965	0.966	0.965±0.002	12.27

Appendix 2-4: Effect of equilibrium solution pH on arsenate (As(V)) adsorption onto **Iron oxide coated powdered activated carbon** (experiment condition employed: Initial concentration 1.0 mg/L as AsO₄, adsorbent dosage 5 g/L, adsorption time 24 hours).

Mass (g/L)	pH _I	pH _F	Initial conc (mg/L)	Final concentration (mg/L)				%R As
				1	2	3	Avg ± SD	
5.0	2.01	2.08	0.967	0.035	0.036	0.036	0.036±0.001	96.28
5.0	3.06	3.09	1.040	0.025	0.025	0.026	0.025±0.001	97.64
5.0	4.03	4.03	1.050	0.005	0.005	0.005	0.005±0.000	99.52
5.0	5.06	5.01	1.090	0.027	0.028	0.029	0.028±0.001	97.43
5.0	6.04	5.78	1.150	0.481	0.480	0.479	0.480±0.001	58.26
5.0	7.04	6.85	1.160	0.781	0.780	0.779	0.780±0.001	32.76
5.0	8.04	7.23	1.000	0.743	0.746	0.745	0.745±0.002	25.50
5.0	9.01	8.63	1.120	0.920	0.921	0.920	0.920±0.001	17.86
5.0	10.02	9.68	1.100	0.918	0.921	0.915	0.918±0.003	16.55

Appendix 3-1: Effect of contact time on arsenate (As(V)) adsorption onto **virgin powdered activated carbon** (experiment condition employed: Initial As(V) concentration 1.0 mg/L, adsorbent dosage 5 g/L, solution pH 5.0)

Time (hr)	Initial pH	Final pH	Mass (g)	Vol (L)	Initial concentration (mg/L)	Final Concentration (mg/L)				qt (mg/g)	%R As
						1	2	3	Avg \pm SD		
0.15	5.00	5.01	0.25	0.05	1.180	0.925	0.922	0.928	0.925 \pm 0.003	0.0510	21.61
0.30	5.00	5.01	0.25	0.05	1.180	0.901	0.899	0.903	0.901 \pm 0.002	0.0558	23.64
0.45	5.00	5.01	0.25	0.05	1.180	0.869	0.868	0.879	0.872 \pm 0.006	0.0616	26.10
1	5.00	5.00	0.25	0.05	1.180	0.830	0.831	0.837	0.833 \pm 0.004	0.0694	29.41
2	5.00	5.01	0.25	0.05	1.180	0.795	0.796	0.803	0.798 \pm 0.004	0.0764	32.37
3	5.00	5.01	0.25	0.05	1.180	0.765	0.764	0.765	0.765 \pm 0.001	0.0830	35.17
4	5.00	5.02	0.25	0.05	1.180	0.731	0.732	0.735	0.733 \pm 0.002	0.0894	37.88
5	5.00	5.01	0.25	0.05	1.180	0.741	0.716	0.714	0.715 \pm 0.001	0.0930	39.41
6	5.00	5.00	0.25	0.05	1.180	0.693	0.632	0.697	0.694 \pm 0.04	0.0972	41.19
10	5.00	5.01	0.25	0.05	1.180	0.655	0.656	0.662	0.658 \pm 0.004	0.1044	44.24
12	5.00	5.02	0.25	0.05	1.180	0.651	0.655	0.654	0.653 \pm 0.002	0.1054	44.66
16	5.00	5.01	0.25	0.05	1.180	0.646	0.642	0.656	0.648 \pm 0.007	0.1064	45.08
20	5.00	5.03	0.25	0.05	1.180	0.640	0.641	0.642	0.641 \pm 0.001	0.1078	45.68
24	5.00	5.02	0.25	0.05	1.180	0.631	0.638	0.635	0.635 \pm 0.004	0.1090	46.19

Appendix 3-2: Effect of contact time on arsenate (As(V)) adsorption onto **virgin granular activated carbon** (experiment condition employed: Initial As(V) concentration 1.0 mg/L, adsorbent dosage 5 g/L, solution pH 5.0)

Time (hr)	Initial pH	Final pH	Mass (g)	Vol (L)	Initial concentration (mg/L)	Final Concentration (mg/L)				qt (mg/g)	%R As
						1	2	3	Avg \pm SD		
0.15	5.00	5.00	0.25	0.05	1.180	1.106	1.103	1.104	1.104 \pm 0.002	0.0160	6.78
0.30	5.00	5.00	0.25	0.05	1.180	1.053	1.057	1.055	1.055 \pm 0.002	0.0260	11.02
0.45	5.00	5.00	0.25	0.05	1.180	1.011	1.010	1.010	1.010 \pm 0.001	0.0340	14.41
1	5.00	5.00	0.25	0.05	1.180	0.964	0.971	0.958	0.964 \pm 0.007	0.0440	18.64
2	5.00	5.00	0.25	0.05	1.180	0.906	0.909	0.912	0.909 \pm 0.003	0.0540	22.88
3	5.00	5.01	0.25	0.05	1.180	0.874	0.878	0.879	0.877 \pm 0.003	0.0620	26.27
4	5.00	5.01	0.25	0.05	1.180	0.846	0.844	0.849	0.849 \pm 0.003	0.0680	28.81
5	5.00	5.01	0.25	0.05	1.180	0.791	0.819	0.811	0.811 \pm 0.014	0.0740	31.36
6	5.00	5.01	0.25	0.05	1.180	0.785	0.786	0.799	0.790 \pm 0.008	0.0780	33.05
10	5.00	5.00	0.25	0.05	1.180	0.736	0.742	0.739	0.739 \pm 0.003	0.0880	37.29
12	5.00	5.02	0.25	0.05	1.180	0.722	0.718	0.717	0.719 \pm 0.003	0.0922	39.07
16	5.00	5.01	0.25	0.05	1.180	0.703	0.705	0.707	0.705 \pm 0.002	0.0950	40.25
20	5.00	5.00	0.25	0.05	1.180	0.699	0.699	0.697	0.698 \pm 0.001	0.0964	40.85
24	5.00	5.01	0.25	0.05	1.180	0.689	0.693	0.691	0.691 \pm 0.002	0.0978	41.44

Appendix 3-3: Effect of contact time on arsenate (As(V)) adsorption onto **iron oxide coated powdered activated carbon** (experiment condition employed: Initial As(V) concentration 1.0 mg/L, adsorbent dosage 5 g/L, solution pH 5.0)

Time (hr)	Initial pH	Final pH	Mass (g)	Vol (L)	Initial concentration (mg/L)	Final Concentration (mg/L)				q _t (mg/g)	%R As
						1	2	3	Avg ± SD		
0.15	5.00	5.00	0.25	0.05	1.180	0.155	0.157	0.158	0.157±0.002	0.2046	86.69
0.30	5.00	5.01	0.25	0.05	1.180	0.142	0.143	0.143	0.143±0.001	0.2074	87.8 ₈
0.45	5.00	5.01	0.25	0.05	1.180	0.122	0.127	0.126	0.125±0.003	0.2110	89.41
1	5.00	5.00	0.25	0.05	1.180	0.098	0.097	0.098	0.098±0.001	0.2165	91.74
2	5.00	5.00	0.25	0.05	1.180	0.090	0.090	0.091	0.090±0.001	0.2179	92.34
3	5.00	5.03	0.25	0.05	1.180	0.082	0.083	0.093	0.083±0.006	0.2195	92.99
4	5.00	5.00	0.25	0.05	1.180	0.073	0.072	0.072	0.072±0.001	0.2215	93.86
5	5.00	5.00	0.25	0.05	1.180	0.062	0.062	0.062	0.062±0.001	0.2235	94.72
6	5.00	5.00	0.25	0.05	1.180	0.045	0.049	0.056	0.050±0.006	0.2260	95.76
10	5.00	5.00	0.25	0.05	1.180	0.043	0.042	0.043	0.042±0.001	0.2275	96.41
12	5.00	5.04	0.25	0.05	1.180	0.035	0.035	0.0304	0.035±0.001	0.2291	97.07
16	5.00	5.03	0.25	0.05	1.180	0.031	0.031	0.031	0.031±0.001	0.2298	97.36
20	5.00	5.01	0.25	0.05	1.180	0.031	0.029	0.031	0.030±0.001	0.2300	97.46
24	5.00	5.04	0.25	0.05	1.180	0.029	0.029	0.029	0.029±0.001	0.2302	97.54

Appendix 3-4: Effect of contact time on arsenate (As(V)) adsorption onto **iron oxide coated granular activated** carbon (experiment condition employed: Initial As(V) concentration 1.0 mg/L, adsorbent dosage 5 g/L, solution pH 5.0)

Time (hr)	Initial pH	Final pH	Mass (g)	Vol (L)	Initial concentration (mg/L)	Final Concentration (mg/L)				q _t (mg/g)	%R As
						1	2	3	Avg ± SD		
0.15	5.00	5.04	0.25	0.05	1.180	0.885	0.884	0.887	0.887±0.002	0.0586	24.83
0.30	5.00	5.06	0.25	0.05	1.180	0.773	0.771	0.769	0.770±0.002	0.0820	34.75
0.45	5.00	5.06	0.25	0.05	1.180	0.682	0.680	0.681	0.681±0.001	0.0998	42.29
1	5.00	5.07	0.25	0.05	1.180	0.557	0.555	0.554	0.555±0.002	0.1250	52.97
2	5.00	5.07	0.25	0.05	1.180	0.390	0.397	0.398	0.395±0.004	0.1570	66.53
3	5.00	5.21	0.25	0.05	1.180	0.324	0.318	0.319	0.320±0.003	0.1720	72.88
4	5.00	5.17	0.25	0.05	1.180	0.278	0.277	0.277	0.277±0.001	0.1806	76.53
5	5.00	5.18	0.25	0.05	1.180	0.247	0.244	0.243	0.245±0.002	0.1870	79.24
6	5.00	5.21	0.25	0.05	1.180	0.215	0.217	0.216	0.216±0.001	0.1928	81.69
10	5.00	5.22	0.25	0.05	1.180	0.155	0.154	0.155	0.155±0.001	0.2050	86.86
12	5.00	5.23	0.25	0.05	1.180	0.116	0.120	0.118	0.118±0.002	0.2124	90.00
16	5.00	5.23	0.25	0.05	1.180	0.082	0.086	0.087	0.085±0.003	0.2190	92.80
20	5.00	5.20	0.25	0.05	1.180	0.075	0.074	0.074	0.075±0.001	0.2211	93.69
24	5.00	5.20	0.25	0.05	1.180	0.065	0.065	0.065	0.065±0.001	0.2230	94.48

Appendix 4-1: Adsorption kinetic on arsenate (As(V)) adsorption on **virgin powdered activated carbon**.

Time (hr)	Mass (g)	Vol (L)	Initial concentration (mg/L)	Final concentration (mg/L)	q_t (mg/g)	q_e (mg/L)	Pseudo 1 st order		Pseudo 2 nd order
							$q_e - q_t$	$\log(q_e - q_t)$	
0.15	0.25	0.05	1.180	0.925	0.0510	0.106	0.0554	-1.2565	2.941
0.30	0.25	0.05	1.180	0.901	0.0558	0.106	0.0506	-1.2958	5.376
0.45	0.25	0.05	1.180	0.872	0.0616	0.106	0.0448	-1.3487	7.305
1	0.25	0.05	1.180	0.833	0.0694	0.106	0.0370	-1.4318	14.409
2	0.25	0.05	1.180	0.798	0.0764	0.106	0.0300	-1.5229	26.178
3	0.25	0.05	1.180	0.765	0.0830	0.106	0.0234	-1.6308	36.145
4	0.25	0.05	1.180	0.733	0.0894	0.106	0.0170	-1.7696	44.743
5	0.25	0.05	1.180	0.715	0.0930	0.106	0.0134	-1.8729	53.763
6	0.25	0.05	1.180	0.694	0.0972	0.106	0.0092	-2.0362	61.728
10	0.25	0.05	1.180	0.658	0.1044	0.106	0.0020	-2.6990	95.785
12	0.25	0.05	1.180	0.653	0.1054	0.106	0.0010	-3.0000	113.852
16	0.25	0.05	1.180	0.648	0.1064	0.106	0.0000	#NUM!	150.376
20	0.25	0.05	1.180	0.641	0.1078	0.106	-0.0014	#NUM!	185.529
24	0.25	0.05	1.180	0.635	0.1090	0.106	-0.0026	#NUM!	220.183

Appendix 4-2: Adsorption kinetic on arsenate (As(V)) adsorption on **virgin granular activated carbon**.

Time (hr)	Mass (g)	Vol (L)	Initial concentration (mg/L)	Final concentration (mg/L)	q_t (mg/g)	q_e (mg/L)	Pseudo 1 st order		Pseudo 2 nd order
							$q_e - q_t$	$\log(q_e - q_t)$	
0.15	0.25	0.05	1.180	1.104	0.0160	0.095	0.0790	-1.1024	9.375
0.30	0.25	0.05	1.180	1.055	0.0260	0.095	0.0690	-1.1612	11.538
0.45	0.25	0.05	1.180	1.010	0.0340	0.095	0.0610	-1.2147	13.235
1	0.25	0.05	1.180	0.964	0.0440	0.095	0.0510	-1.2924	22.727
2	0.25	0.05	1.180	0.909	0.0540	0.095	0.0410	-1.3872	37.037
3	0.25	0.05	1.180	0.877	0.0620	0.095	0.0330	-1.4815	48.387
4	0.25	0.05	1.180	0.849	0.0680	0.095	0.0270	-1.5686	58.824
5	0.25	0.05	1.180	0.811	0.0740	0.095	0.0210	-1.6778	67.568
6	0.25	0.05	1.180	0.790	0.0780	0.095	0.0170	-1.7696	76.923
10	0.25	0.05	1.180	0.739	0.0880	0.095	0.0070	-2.1549	113.636
12	0.25	0.05	1.180	0.719	0.0922	0.095	0.0028	-2.5528	130.152
16	0.25	0.05	1.180	0.705	0.0950	0.095	0.0000	#NUM!	168.421
20	0.25	0.05	1.180	0.698	0.0964	0.095	-0.0014	#NUM!	207.469
24	0.25	0.05	1.180	0.691	0.0978	0.095	-0.0028	#NUM!	245.399

Appendix 4-3: Adsorption kinetic on arsenate (As(V)) adsorption on **iron oxide coated powdered activated carbon.**

Time (hr)	Mass (g)	Vol (L)	Initial concentration (mg/L)	Final concentration (mg/L)	q_t (mg/g)	q_e (mg/L)	Pseudo 1 st order		Pseudo 2 nd order
							$q_e - q_t$	$\log(q_e - q_t)$	
0.15	0.25	0.05	1.180	0.157	0.2046	0.230	0.0252	-1.5993	0.733
0.30	0.25	0.05	1.180	0.143	0.2074	0.230	0.0224	-1.6505	1.446
0.45	0.25	0.05	1.180	0.125	0.2110	0.230	0.0188	-1.7268	2.133
1	0.25	0.05	1.180	0.098	0.2165	0.230	0.0133	-1.8775	4.619
2	0.25	0.05	1.180	0.090	0.2179	0.230	0.0118	-1.9266	9.178
3	0.25	0.05	1.180	0.083	0.2195	0.230	0.0103	-1.9872	13.670
4	0.25	0.05	1.180	0.072	0.2215	0.230	0.0082	-2.0841	18.057
5	0.25	0.05	1.180	0.062	0.2231	0.230	0.0067	-2.1752	22.413
6	0.25	0.05	1.180	0.050	0.2262	0.230	0.0035	-2.4510	26.523
10	0.25	0.05	1.180	0.042	0.2275	0.230	0.0022	-2.6498	43.952
12	0.25	0.05	1.180	0.035	0.2284	0.230	0.0014	-2.8665	52.539
16	0.25	0.05	1.180	0.031	0.2298	0.230	0.0000	#NUM!	69.638
20	0.25	0.05	1.180	0.030	0.2302	0.230	-0.0005	#NUM!	86.873
24	0.25	0.05	1.180	0.029	0.2318	0.230	-0.0020	#NUM!	103.538

Appendix 4-4: Adsorption kinetic on arsenate (As(V)) adsorption on **iron oxide coated granular activated carbon**.

Time (hr)	Mass (g)	Vol (L)	Initial concentration (mg/L)	Final concentration (mg/L)	q_t (mg/g)	q_e (mg/L)	Pseudo 1 st order		Pseudo 2 nd order
							$q_e - q_t$	$\log(q_e - q_t)$	
0.15	0.25	0.05	1.180	0.887	0.0586	0.219	0.1604	-0.7948	2.560
0.30	0.25	0.05	1.180	0.770	0.0820	0.219	0.1370	-0.8633	3.659
0.45	0.25	0.05	1.180	0.681	0.0998	0.219	0.1192	-0.9237	4.509
1	0.25	0.05	1.180	0.555	0.1250	0.219	0.0940	-1.0269	8.00
2	0.25	0.05	1.180	0.395	0.1570	0.219	0.0620	-1.2076	12.739
3	0.25	0.05	1.180	0.320	0.1720	0.219	0.0470	-1.3279	17.442
4	0.25	0.05	1.180	0.277	0.1806	0.219	0.0384	-1.4157	22.148
5	0.25	0.05	1.180	0.245	0.1870	0.219	0.0320	-1.4949	26.738
6	0.25	0.05	1.180	0.216	0.1928	0.219	0.0262	-1.5817	31.120
10	0.25	0.05	1.180	0.155	0.2050	0.219	0.0140	-1.8539	48.780
12	0.25	0.05	1.180	0.118	0.2124	0.219	0.0066	-2.1805	56.497
16	0.25	0.05	1.180	0.085	0.2190	0.219	0.0000	#NUM!	73.059
20	0.25	0.05	1.180	0.075	0.2211	0.219	-0.002	#NUM!	90.457
24	0.25	0.05	1.180	0.065	0.2230	0.219	-0.004	#NUM!	107.633

Appendix 5-1: Effect of adsorbent dosage on arsenate (As(V)) adsorption on **virgin powdered activated carbon** (experiment condition employed: Initial As(V) concentration 1.0 mg/L, solution pH 5.0, adsorption time 16 hours)

Mass (g)	Vol (L)	Initial Conc (mg/L)	Final Concentration (mg/L)			C _t /C _o (mg/L)	q _t (mg/g)	%R As
			1	2	Avg ± SD			
0.05	0.05	1.100	0.992	0.998	0.995±0.004	0.904	0.105	9.55
0.10	0.05	1.100	0.942	0.938	0.940±0.003	0.854	0.08	14.55
0.15	0.05	1.100	0.844	0.836	0.840±0.003	0.764	0.087	23.64
0.20	0.05	1.100	0.689	0.690	0.690±0.001	0.627	0.1025	37.27
0.25	0.05	1.100	0.621	0.619	0.620±0.001	0.563	0.096	43.64
0.30	0.05	1.100	0.587	0.583	0.585±0.003	0.532	0.0858	46.82

Appendix 5-2: Effect of adsorbent dosage on arsenate (As(V)) adsorption on **virgin granular activated carbon** (experiment condition employed: Initial As(V) concentration 1.0 mg/L, solution pH 5.0, adsorption time 16 hours)

Mass (g)	Vol (L)	Initial Conc (mg/L)	Final Concentration (mg/L)			C _t /C _o (mg/L)	q _t (mg/g)	%R As
			1	2	Avg ± SD			
0.05	0.05	1.100	1.024	1.035	1.030±0.008	0.936	0.07	6.36
0.10	0.05	1.100	0.974	0.986	0.970±0.008	0.881	0.065	11.82
0.15	0.05	1.100	0.871	0.869	0.870±0.001	0.791	0.076	20.91
0.20	0.05	1.100	0.732	0.728	0.730±0.003	0.664	0.092	33.64
0.25	0.05	1.100	0.652	0.648	0.650±0.003	0.591	0.09	40.91
0.30	0.05	1.100	0.627	0.633	0.630±0.004	0.573	0.078	42.73

Appendix 5-3: Effect of adsorbent dosage on arsenate (As(V)) adsorption on **iron oxide coated powdered activated carbon** (experiment condition employed: Initial As(V) concentration 1.0 mg/L, solution pH 5.0, adsorption time 16 hours).

Mass (g)	Vol (L)	Initial Conc (mg/L)	Final Concentration (mg/L)			C _t /C _o (mg/L)	q _t (mg/g)	%R As
			1	2	Avg ± SD			
0.05	0.05	1.100	0.405	0.403	0.404±0.001	0.3673	0.696	63.27
0.10	0.05	1.100	0.257	0.256	0.257±0.001	0.2336	0.422	76.64
0.15	0.05	1.100	0.161	0.168	0.165±0.005	0.1500	0.312	85.00
0.20	0.05	1.100	0.099	0.100	0.100±0.001	0.0909	0.250	90.91
0.25	0.05	1.100	0.025	0.032	0.029±0.005	0.0262	0.214	97.38
0.30	0.05	1.100	0.019	0.023	0.021±0.003	0.0186	0.180	98.14

Appendix 5-4: Effect of adsorbent dosage on arsenate (As(V)) adsorption on **iron oxide coated granular activated carbon** (experiment condition employed: Initial As(V) concentration 1.0 mg/L, solution pH 5.0, adsorption time 16 hours)

Mass (g)	Vol (L)	Initial Conc (mg/L)	Final Concentration (mg/L)			C _t /C _o (mg/L)	q _t (mg/g)	%R As
			1	2	Avg ± SD			
0.05	0.05	1.100	0.657	0.646	0.652±0.008	0.592	0.448	40.73
0.10	0.05	1.100	0.507	0.503	0.505±0.003	0.459	0.298	54.09
0.15	0.05	1.100	0.340	0.349	0.345±0.006	0.313	0.252	68.64
0.20	0.05	1.100	0.217	0.218	0.218±0.001	0.198	0.220	80.18
0.25	0.05	1.100	0.081	0.079	0.080±0.001	0.073	0.204	92.73
0.30	0.05	1.100	0.043	0.047	0.045±0.003	0.041	0.176	95.91

Appendix 6-1: Adsorption isotherm on arsenate (As(V)) adsorption on **virgin powdered activated carbon**.

Co (mg/L)	Ce (mg/L)	C (mg/L)	X (mg)	x/m (mg/g)	Log (Ce)	Log (q)	Ce/qe (g/L)
1.100	0.995	0.11	0.0053	0.1050	-0.00217	-0.9788	9.476
1.100	0.94	0.16	0.0080	0.0800	-0.02687	-1.0969	11.75
1.100	0.84	0.26	0.0130	0.0867	-0.07572	-1.0621	9.692
1.100	0.69	0.41	0.0205	0.1025	-0.16115	-0.9893	6.731
1.100	0.62	0.48	0.0240	0.0960	-0.20760	-1.0177	6.458
1.100	0.585	0.52	0.02575	0.08583	-0.23284	-1.0663	6.815

Appendix 6-2: Adsorption isotherm on arsenate (As(V)) adsorption on **virgin granular activated carbon**.

Co (mg/L)	Ce (mg/L)	C (mg/L)	X (mg)	x/m (mg/g)	Log (Ce)	Log (q)	Ce/qe (g/L)
1.100	1.03	0.07	0.0035	0.0700	0.01283	-1.1549	14.714
1.100	0.97	0.13	0.0065	0.0650	-0.01323	-1.1870	14.923
1.100	0.87	0.23	0.0115	0.0767	-0.06048	-1.1153	11.347
1.100	0.73	0.37	0.0185	0.0925	-0.13667	-1.0338	7.891
1.100	0.65	0.45	0.0225	0.0900	-0.18708	-1.0457	7.222
1.100	0.63	0.47	0.0235	0.0783	-0.20065	-1.1060	8.042

Appendix 6-3: Adsorption isotherm on arsenate (As(V)) adsorption on **iron oxide coated powdered activated carbon.**

Co (mg/L)	Ce (mg/L)	C (mg/L)	X (mg)	x/m (mg/g)	Log (Ce)	Log (q)	Ce/qe (g/L)
1.100	0.404	0.70	0.03480	0.696	-0.39361	-0.1574	0.5805
1.100	0.257	0.84	0.04215	0.4215	-0.59006	-0.3752	0.6097
1.100	0.165	0.94	0.04675	0.3116	-0.78251	-0.5063	0.5294
1.100	0.1	1.00	0.05000	0.25	-1	-0.6021	0.4
1.100	0.0288	1.07	0.05356	0.2142	-1.54060	-0.6691	0.1344
1.100	0.0205	1.08	0.05398	0.1799	-1.68824	-0.7449	0.1139

Appendix 6-4: Adsorption isotherm on arsenate (As(V)) adsorption on **iron oxide coated granular activated carbon.**

Co (mg/L)	Ce (mg/L)	C (mg/L)	X (mg)	x/m (mg/g)	Log (Ce)	Log (q)	Ce/qe (g/L)
1.100	0.652	0.45	0.0224	0.448	-0.18575	-0.3487	1.4554
1.100	0.505	0.60	0.02975	0.2975	-0.29670	-0.5265	1.6975
1.100	0.345	0.76	0.03775	0.252	-0.46218	-0.5992	1.3709
1.100	0.218	0.88	0.04410	0.2205	-0.66154	-0.6566	0.9887
1.100	0.08	1.02	0.05100	0.204	-1.09691	-0.6904	0.3922
1.100	0.045	1.06	0.05275	0.176	-1.34678	-0.7549	0.2559

Appendix 7: Effect of ionic strength on arsenate (As(V)) adsorption onto **Virgin powdered activated carbon, Virgin granular activated carbon, iron oxide coated powdered activated carbon and iron oxide coated granular activated carbon** (experiment condition employed: Initial As(V) concentration 1.0 mg/L, solution pH 5.0, adsorption time 16 hours with adsorbent dosage 5.0 g/L)

Type	Mass (g)	Vol (L)	Ionic strength (M)	Initial Concentration (mg/L)	Final Concentration (mg/L)	%Removal As
					Avg \pm SD	
Fe(II) GAC	0.25	0.05	0.00	0.977	0.081 \pm 0.002	91.64
	0.25	0.05	0.01	0.899	0.058 \pm 0.003	93.57
	0.25	0.05	0.10	0.811	0.067 \pm 0.002	91.78
Fe(II) PAC	0.25	0.05	0.00	0.977	0.014 \pm 0.002	98.58
	0.25	0.05	0.01	0.899	0.006 \pm 0.001	99.34
	0.25	0.05	0.10	0.811	0.006 \pm 0.000	99.26
Virgin PAC	0.25	0.05	0.00	0.977	0.532 \pm 0.001	45.55
	0.25	0.05	0.01	0.899	0.471 \pm 0.001	47.61
	0.25	0.05	0.10	0.811	0.430 \pm 0.001	46.98
Virgin GAC	0.25	0.05	0.00	0.977	0.589 \pm 0.002	39.71
	0.25	0.05	0.01	0.899	0.530 \pm 0.002	41.05
	0.25	0.05	0.10	0.811	0.480 \pm 0.002	40.81

Appendix 8: Effect of co-existing ion on arsenate (As(V)) adsorption onto **virgin powdered activated carbon (i), virgin granular activated carbon (ii), iron oxide coated powdered activated carbon (iii) and iron oxide coated granular activated carbon (iv)** (experiment condition employed: Initial As(V) concentration 1.0 mg/L and 5.0 mg/L as FeSO₄, solution pH 5.0, adsorption time 16 hours with adsorbent dosage 5.0 g/L)

Type	Mass (g/L)	Vol (L)	Initial Concentration (mg/L)	Final Concentration (mg/L)	Ionic strength (M)	%Removal As
Fe(II) GAC	5.0	0.05	0.899	0.195	0.01	70.4
Fe(II) PAC	5.0	0.05	0.899	0.132	0.01	76.7
Virgin GAC	5.0	0.05	0.899	0.665	0.01	23.4
Virgin PAC	5.0	0.05	0.899	0.600	0.01	29.9



Appendix 9: The arsenate (As(V)) adsorption efficiency onto iron oxide coated granular activated carbon in **Rapid Lab Scale Column**. (experiment employed: Initial concentration of 1.0 mg/L as AsO₄, solution pH 5.0, fixed bed 5.0 g, flow rate 1 mL/min)

Time (min)	Volume (L)	Mass (g)	Initial concentration (mg/L)	Final concentration (mg/L)	Ct/Co (mg/L)	%Removal As(V)
30	0.030	5.0	1.200	0.00156	0.0013	99.87
60	0.060	5.0	1.200	0.00242	0.0020	99.80
90	0.090	5.0	1.200	0.00277	0.0023	99.77
120	0.120	5.0	1.200	0.0031	0.0026	99.74
150	0.150	5.0	1.200	0.00345	0.0029	99.71
180	0.180	5.0	1.200	0.00518	0.0043	99.57
210	0.210	5.0	1.200	0.00619	0.0052	99.45
240	0.240	5.0	1.200	0.00657	0.0055	99.45
270	0.270	5.0	1.200	0.00969	0.0081	99.19
300	0.300	5.0	1.200	0.01490	0.0124	98.76
330	0.330	5.0	1.200	0.03930	0.0328	96.72
360	0.360	5.0	1.200	0.04760	0.0397	96.03
720	0.720	5.0	1.200	0.24700	0.2058	79.42
960	0.960	5.0	1.200	0.41800	0.3483	65.17
1200	1.200	5.0	1.200	0.49600	0.4133	58.67
1440	1.440	5.0	1.200	0.60600	0.5050	49.5
1920	1.920	5.0	1.200	0.65300	0.5442	45.58
2400	2.400	5.0	1.200	0.68100	0.5675	43.25
2880	2.880	5.0	1.200	0.69000	0.5750	42.5
3360	3.360	5.0	1.200	0.71700	0.5975	40.25
3840	3.840	5.0	1.200	0.73500	0.6125	38.75
4320	4.320	5.0	1.200	0.76300	0.6358	36.42
4800	4.800	5.0	1.200	0.81000	0.6750	32.5
5280	5.280	5.0	1.200	0.84900	0.7075	29.25
5760	5.760	5.0	1.200	0.95400	0.7950	20.5
6240	6.240	5.0	1.200	0.98200	0.8183	18.17
6720	6.720	5.0	1.200	1.03000	0.8583	14.17
7200	7.200	5.0	1.200	1.11000	0.9250	7.5

Appendix 10: **Thomas modelling** for analytical result on arsenate (As(V)) adsorption onto iron oxide coated granular activated carbon.

Time (min)	Volume (L)	Initial concentration (mg/L)	Final concentration (mg/L)	Co/Ct (mg/L)	(Co/Ct - 1)	ln (Co/Ct -1)
30	0.030	1.200	0.00156	769.23	768.23	6.64
60	0.060	1.200	0.00242	495.87	494.87	6.20
90	0.090	1.200	0.00277	433.21	432.21	6.07
120	0.120	1.200	0.00310	387.10	386.10	5.96
150	0.150	1.200	0.00345	347.83	346.83	5.85
180	0.180	1.200	0.00518	231.66	230.66	5.44
210	0.210	1.200	0.00619	193.86	192.86	5.26
240	0.240	1.200	0.00657	182.65	181.65	5.20
270	0.270	1.200	0.00969	123.84	122.84	4.81
300	0.300	1.200	0.01490	80.54	79.54	4.38
330	0.330	1.200	0.03930	30.53	29.53	3.39
360	0.360	1.200	0.04760	25.21	24.21	3.19
720	0.720	1.200	0.24700	4.86	3.86	1.35
960	0.960	1.200	0.41800	2.87	1.87	0.63
1200	1.200	1.200	0.49600	2.42	1.42	0.35
1440	1.440	1.200	0.60600	1.98	0.98	-0.02
1920	1.920	1.200	0.65300	1.84	0.84	-0.18
2400	2.400	1.200	0.68100	1.76	0.76	-0.27
2880	2.880	1.200	0.69000	1.74	0.74	-0.30
3360	3.360	1.200	0.71700	1.67	0.67	-0.40
3840	3.840	1.200	0.73500	1.63	0.63	-0.46
4320	4.320	1.200	0.76300	1.57	0.57	-0.56
4800	4.800	1.200	0.81000	1.48	0.48	-0.73
5280	5.280	1.200	0.84900	1.41	0.41	-0.88
5760	5.760	1.200	0.95400	1.26	0.26	-1.36
6240	6.240	1.200	0.98200	1.22	0.22	-1.51
6720	6.720	1.200	1.03000	1.17	0.17	-1.80
7200	7.200	1.200	1.11000	1.08	0.08	-2.51

Appendix 11: **Adams-Bohart modelling** for analytical result on arsenate (As(V)) adsorption onto iron oxide coated granular activated carbon.

Time (min)	Volume (L)	Initial concentration (mg/L)	Final concentration (mg/L)	Ct/Co (mg/L)	ln (Ct/Co)
30	0.030	1.200	0.00156	0.001	-6.645
60	0.060	1.200	0.00242	0.002	-6.206
90	0.090	1.200	0.00277	0.002	-6.071
120	0.120	1.200	0.00310	0.003	-5.959
150	0.150	1.200	0.00345	0.003	-5.852
180	0.180	1.200	0.00518	0.004	-5.445
210	0.210	1.200	0.00619	0.005	-5.267
240	0.240	1.200	0.00657	0.005	-5.208
270	0.270	1.200	0.00969	0.008	-4.819
300	0.300	1.200	0.01490	0.012	-4.389
330	0.330	1.200	0.03930	0.033	-3.419
360	0.360	1.200	0.04760	0.040	-3.227
720	0.720	1.200	0.24700	0.206	-1.581
960	0.960	1.200	0.41800	0.348	-1.055
1200	1.200	1.200	0.49600	0.413	-0.884
1440	1.440	1.200	0.60600	0.505	-0.683
1920	1.920	1.200	0.65300	0.544	-0.608
2400	2.400	1.200	0.68100	0.568	-0.567
2880	2.880	1.200	0.69000	0.575	-0.553
3360	3.360	1.200	0.71700	0.598	-0.515
3840	3.840	1.200	0.73500	0.613	-0.490
4320	4.320	1.200	0.76300	0.636	-0.453
4800	4.800	1.200	0.81000	0.675	-0.393
5280	5.280	1.200	0.84900	0.708	-0.346
5760	5.760	1.200	0.95400	0.795	-0.229
6240	6.240	1.200	0.98200	0.818	-0.200
6720	6.720	1.200	1.03000	0.858	-0.153
7200	7.200	1.200	1.11000	0.925	-0.078

Appendix 12: **Yoon-Nelson modelling** for analytical result on arsenate (As(V)) adsorption onto iron oxide coated granular activated carbon.

Time (min)	Volume (L)	Initial concentration (mg/L)	Final concentration (mg/L)	Co - Ct (mg/L)	Ct/(Co-Ct)	ln(Ct/(Co-Ct))
30	0.030	1.200	0.00156	1.198	0.0013	-6.644
60	0.060	1.200	0.00242	1.197	0.0020	-6.204
90	0.090	1.200	0.00277	1.197	0.0023	-6.068
120	0.120	1.200	0.00310	1.197	0.0026	-5.956
150	0.150	1.200	0.00345	1.196	0.0029	-5.848
180	0.180	1.200	0.00518	1.195	0.0043	-5.440
210	0.210	1.200	0.00619	1.194	0.0052	-5.261
240	0.240	1.200	0.00657	1.193	0.0055	-5.202
270	0.270	1.200	0.00969	1.190	0.0081	-4.810
300	0.300	1.200	0.01490	1.185	0.0125	-4.376
330	0.330	1.200	0.03930	1.160	0.0338	-3.385
360	0.360	1.200	0.04760	1.152	0.041	-3.186
720	0.720	1.200	0.24700	0.953	0.259	-1.350
960	0.960	1.200	0.41800	0.782	0.534	-0.626
1200	1.200	1.200	0.49600	0.704	0.704	-0.350
1440	1.440	1.200	0.60600	0.594	1.020	0.020
1920	1.920	1.200	0.65300	0.547	1.193	0.177
2400	2.400	1.200	0.68100	0.519	1.3102	0.271
2880	2.880	1.200	0.69000	0.51	1.3525	0.302
3360	3.360	1.200	0.71700	0.483	1.484	0.395
3840	3.840	1.200	0.73500	0.465	1.580	0.457
4320	4.320	1.200	0.76300	0.437	1.745	0.557
4800	4.800	1.200	0.81000	0.39	2.077	0.730
5280	5.280	1.200	0.84900	0.351	2.418	0.883
5760	5.760	1.200	0.95400	0.246	3.878	1.355
6240	6.240	1.200	0.98200	0.218	4.504	1.505
6720	6.720	1.200	1.03000	0.17	6.058	1.801
7200	7.200	1.200	1.11000	0.09	12.33	2.512

Appendix 13: Effect of regeneration of iron oxide coated granular activated carbon on Arsenate (As(V)) adsorption in **Rapid Lab Scale Column** (experiment employed: Initial concentration of 1.0 mg/L as AsO₄, solution pH 5.0, fixed bed 5.0 g, flow rate 1 mL/min).

Time (hr)	Initial Concentration (mg/L)	1 st generation		2 nd generation		3 rd generation	
		Final _{conc}	%R	Final _{conc}	%R	Final _{conc}	%R
30	1.200	0.0024	99.80	0.0037	99.70	0.0061	99.49
60	1.200	0.0036	99.70	0.0044	99.64	0.0089	99.26
90	1.200	0.0042	99.65	0.0048	99.69	0.0123	98.97
120	1.200	0.0061	99.49	0.0061	99.49	0.0195	98.38
150	1.200	0.0062	99.49	0.0067	99.44	0.0267	97.78
180	1.200	0.0069	99.42	0.0071	99.41	0.0349	97.09
210	1.200	0.0072	99.40	0.0080	99.33	0.0453	96.22
240	1.200	0.0085	99.29	0.0093	99.23	0.0587	95.11
270	1.200	0.0124	98.97	0.0178	98.52	0.0712	94.07
300	1.200	0.0219	98.18	0.0341	97.16	0.0886	92.62
330	1.200	0.0461	96.16	0.0736	93.87	0.1223	89.81
360	1.200	0.0565	95.29	0.1140	90.50	0.1589	89.76
720	1.200	0.2880	76.00	0.3650	69.58	0.5680	52.67
960	1.200	0.4710	60.75	0.5680	52.67	0.6780	43.50

Appendix 13-1: Effect of regeneration of iron oxide coated granular activated carbon on Arsenate (As(V)) adsorption in **Rapid Lab Scale Column** (experiment employed: Initial concentration of 1.0 mg/L as AsO₄, solution pH 5.0, fixed bed 5.0 g, flow rate 1 mL/min).

Time (hr)	Initial Concentration (mg/L)	1 st generation		2 nd generation		3 rd generation	
		Final _{conc}	%R	Final _{conc}	%R	Final _{conc}	%R
1200	1.200	0.537	55.25	0.642	46.50	0.763	36.42
1440	1.200	0.654	45.50	0.703	41.42	0.943	21.42
1920	1.200	0.691	42.42	0.748	37.67	1.2	0.00
2400	1.200	0.712	40.67	0.826	31.17	1.2	0.00
2880	1.200	0.743	38.08	0.880	26.67	1.2	0.00
3360	1.200	0.802	33.17	0.935	22.08	1.2	0.00
3840	1.200	0.845	29.58	0.983	18.08	1.2	0.00
4320	1.200	0.899	25.08	1.15	4.17	1.2	0.00
4800	1.200	0.932	22.33	1.2	0.00	1.2	0.00
5280	1.200	0.968	19.33	1.2	0.00	1.2	0.00
5760	1.200	1.01	15.83	1.2	0.00	1.2	0.00
6240	1.200	1.12	6.67	1.2	0.00	1.2	0.00
6720	1.200	1.2	0.00	1.2	0.00	1.2	0.00
7200	1.200	1.2	0.00	1.2	0.00	1.2	0.00

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