การปรับปรุงคุณภาพของแร่ดินเบาด้วยการเผาเพื่อใช้เป็นตัวดูดซับอาร์เซนิกออกจากน้ำที่ปนเปื้อน

นางสาว มธุรส แสงไพโรจน์

DIATOMITE QUALITY IMPROVEMENT BY CALCINATION FOR REMOVAL OF ARSENIC FROM

CONTAMINATED WATER

Miss Mathuros Sangpairoj

A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Science Program in Environmental Science
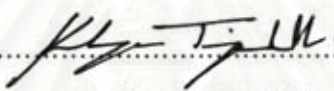
(Interdisciplinary Program)

Graduate School

Chulalongkorn University

Academic Year 2006
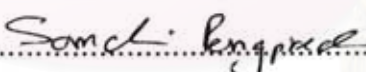
Thesis Title   DIATOMITE QUALITY IMPROVEMENT BY CALCINATION FOR
                    REMOVAL OF ARSENIC FROM CONTAMINATED WATER
By   Miss Mathuros Sangpairoj
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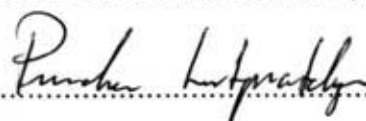
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มธุรส แสงไพโรจน์ : การปรับปรุงคุณภาพของแร่ดินเบาด้วยการเผาเพื่อใช้เป็นตัวดูดซับอาร์เซนิก ออกจากน้ำที่ปนเปื้อน (DIATOMITE QUALITY IMPROVEMENT BY CALCINATION FOR REMOVAL OF ARSENIC FROM CONTAMINATED WATER). อ.ที่ปรึกษา รศ.ดร. สมใจ เพ็งปรีชา, อ.ที่ปรึกษาร่วม: ดร. ปารมี เพ็งปรีชา, 117หน้า.

ในการวิจัยนี้มีจุดประสงค์เพื่อศึกษาความเป็นไปได้ของแร่ดินเบาที่ถูกปรับปรุงคุณภาพสำหรับ กำจัดอาร์เซไนต์ และ อาร์เซเนต ดินเบาถูกปรับปรุงคุณภาพโดยวิธีการเผาที่อุณหภูมิ และ เวลาที่แตกต่างกัน ถูกนำมาศึกษาประสิทธิภาพการกำจัดอาร์เซไนต์และอาร์เซเนตในการทดสอบแบบไม่ต่อเนื่อง   การศึกษา สภาวะที่เหมาะสมได้แก่ ความเข้มข้นของสารละลายอาร์เซไนต์ และ สารละลายอาร์เซเนต, ค่าพีเอช, เวลาสัมผัส, ปริมาณของแร่ดินเบา   และ ศึกษาผลของประจุลบอื่นที่รบกวนการดูดซับ รวมถึง การศึกษาไอโซเทอมการดูดซับแบบฟรุนดลิชและแบบแลงมัวร์   จากนั้นศึกษาประสิทธิภาพการกำจัด อาร์เซนิกในน้ำเสียจริงที่มีการปนเปื้อนของอาร์เซนิกโดยนำแร่ดินเบาที่เหมาะสมมาใช้ในการศึกษา

ผลการศึกษาแสดงว่าแร่ดินเบาที่ผ่านการเผาที่อุณหภูมิ 400 องศาเซลเซียส เป็นเวลา 6 ชั่วโมง (CD4006) สามารถดูดซับอาร์เซไนต์ และ แร่ดินเบาที่ผ่านการเผาที่อุณหภูมิ 800 องศาเซลเซียส เป็น เวลา 6 ชั่วโมง (CD8006) สามารถดูดซับอาร์เซเนตได้ โดยสภาวะที่เหมาะสมสำหรับการกำจัดอาร์เซไนต์และ อาร์เซเนตคือ ที่ระดับความเข้มข้นเท่ากับ 10 มิลลิกรัมต่อลิตร พีเอช 5 เวลาสัมผัส 5ชั่วโมง อัตราการเขย่า 180รอบต่อนาที และ ปริมาณตัวดูดซับ CD4006 และ CD8006 เท่ากับ 3 กรัม สามารถกำจัดอาร์เซไนต์และ อาร์เซเนตได้ 98.72% และ99.05%ตามลำดับ   ผลการศึกษาไอโซเทอมพบว่า ตัวดูดซับ CD4006 และ ตัวดูดซับCD8006 มีรูปแบบสมการการดูดซับของอาร์เซไนต์ และ อาร์เซเนตเป็นแบบฟรุนดลิช โดยมีค่า การดูดซับสูงสุด สำหรับอาร์เซไนต์ และ อาร์เซเนตเท่ากับ 1.77 มิลลิกรัมอาร์เซไนต์ ต่อกรัมตัวดูดซับ CD4006 และ 0.55 มิลลิกรัมอาร์เซเนต ต่อกรัมตัวดูดซับ CD8006 การศึกษาผลของประจุลบอื่นที่รบกวนการ ดูดซับ พบว่าฟอสเฟตมีผลต่อการดูดซับอาร์เซไนต์ และ อาร์เซเนตบนตัวดูดซับ CD4006 และ CD8006 สำหรับการทดลองใช้ตัวดูดซับCD4006 และ ตัวดูดซับ CD8006 กำจัดอาร์เซนิกในน้ำเสียจริงที่มีค่าความ เข้มข้นของอาร์เซนิก 1.95 มิลลิกรัมต่อลิตร พบว่าปริมาณตัวดูดซับ CD4006 และ CD8006 0.1 กรัม สามารถกำจัดอาร์เซนิกในน้ำเสียได้มากกว่า 95 % ซึ่งค่าความเข้มข้นของอาร์เซนิกที่เหลือมีค่าไม่เกิน มาตรฐานน้ำดื่มตามที่องค์การอนามัยโลกกำหนด (< 0.01 มิลลิกรัมต่อลิตร)

สาขาวิชา......วิทยาศาสตร์สิ่งแวดล้อม......................	ลายมือชื่อนิสิต....................................
ปีการศึกษา........2549..................................	ลายมือชื่ออาจารย์ที่ปรึกษา......................
	ลายมือชื่ออาจารย์ที่ปรึกษาร่วม................

4689130320: MAJOR OF ENVIRONMENTAL SCIENCE

KEY WORD: DIATOMITE / ARSENITE / ARSENATE / ADSORPTION / ISOTHERM / ANION

MATHUROS SANGPAIROJ: DIATOMITE QUALITY IMPROVEMENT BY CALCINATION FOR REMOVAL OF ARSENIC FROM CONTAMINATED WATER. THESIS ADVISOR: ASSOC. PROF. SOMCHAI PENGPRECHA, Ph.D., THESIS CO - ADVISOR: PARAMEE PENGPRECHA, Ph.D., 117pp.

The purpose of this research was to investigate the possibility of treated diatomite to be used as an adsorbent for As (III) and As (V) removal. In the preparation of treated diatomite adsorbent, two factors of temperature and time for calcination were studied in the batch experiments. The aims of batch experiments were to study the optimum of temperature and time for preparing treated diatomite, concentrations of As (III) and As (V), pH, contact time, amount of treated diatomite and the competing anions. The adsorption equilibrium was studied by the Freundlich and Langmuir isotherm equations. The optimum conditions of treated diatomite and the efficiency of arsenic removal from arsenic contaminated surface water were studied.

The experimental results showed two appropriate adsorbents for removal As (III) and As (V) under the condition of calcinations at 400 $^\circ$C for 6 hours (CD4006) and at 800 $^\circ$C for 6 hours (CD8006). It was found that the efficiency of CD4006 and CD8006 adsorbents for removal As (III) and As (V) depended on pH, contact time and amount of treated diatomite. The optimum conditions for As (III) and As (V) removal were as follows: 10 mg/l of As (III) and As (V) concentrations at pH 5 for 5 hours with shaking rate of 180 rpm and the 3.0 g of CD4006 and CD8006 adsorbents. The efficiency of As (III) and As (V) removal were 98.72 % and 99.05%, respectively. The adsorption isotherm for As (III) and As (V) removal was complied with the Fruendlich isotherm. The maximum capacities of adsorbents were 1.77 mg As (III)/ g CD4006 and 0.55 mg As (V) / g CD8006. For the results of the competing anions, the removal of As (III) and As (V) was affected by phosphate anion.

Using 0.1 g of CD4006 and CD8006 adsorbents for removal arsenic from arsenic contaminated surface water at the concentration of 1.95 mg/l, the arsenic was reduced to < 0.05 mg/l. Therefore, the water quality could meet the discharge standard of Bottled Drinking Water Quality Standards (WHO As maximum allowable 0.01 mg/l).

Field of study.........Environmental Science......... Student's signature....... M. Sanpairoj

Academic year.........2006................................ Advisor's signature.... Somch. Pengprecha

Coadvisor's signature... Pamee Pec

ACKNOWLEDGEMENTS

I would like to express my greatest gratitude to my advisor, Associate Professor Dr. Somchai pengprecha for his kindness, encouraged and guidance throughout this study. I am grateful and appreciation to Dr. Paramee Pengprecha, my co – advisor for her valuable suggestions and leading me to complete this study. In addition, I am also grateful to Assistant Professor Dr. Charnwit Kositanont, as the chairman, Associate Professor Dr. Thares Srisatit and Assistant Professor Dr. Preecha Lertpratchya as the member of thesis committee.

I am thankful to the staffs from the Scientific and Technological Research Equipment center Chulalongkorn University, who facilitated the use of many instruments and have assisted in analyzing the arsenic concentration. I gratefully thank Department of Chemistry for providing the laboratory, chemicals and equipments. Department of Material Science for the use of sieves. Special thanks to officers and many best friends in Environmental Science Interdisciplinary Program who have assisted in all cases and have provided encouragement. I am also thankful to the Faculty of Environmental Engineering Kasetsart University for providing the arsenic contaminated surface water from Ron Pibun Nakorn Si Tammarat province.

I gratefully thank Graduate School, Chulalongkorn University for financial support for this thesis.

Finally, I would like to dedicate this thesis to my parent who has always been the source of my support and encouragement.

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CHAPTER I

INTRODUCTION

Water pollution problems have become more for decades. Many water resources have deteriorated from toxic contaminants as the result of industrial and human activities such as the wastewater from industrial processes, spraying of pesticides, and disposal of industrial and domestic wastes. The most important toxic contaminants are acids and heavy metals such as Cd, As, Zn, Pb, Cr and Hg. These contaminants released to the environment will affect plants, animals, health and welfare of human.

Arsenic is ubiquitously encountered in the environment and well known for its toxicity to human and animal when ingested or inhaled. Arsenic occurs naturally in the earth's crust and is widely distributed in the environment. In natural water, arsenic is primarily presented in inorganic forms and existed in two predominant species, arsenate [As (V)] and arsenite [As (III)]. As (V) is the major arsenic species in surface water, while As (III) is the dominant arsenic in groundwater since it favor under reducing conditions. Arsenic is used in hardening of alloys and in production of semiconductors, pigments, glass manufacturing, pesticides, rodenticides and fungicides (Shevade and Ford, 2004). Because of its usefulness and exploitation, arsenic contamination is now widespread in the environment and it exerts a toxic effect in a variety of organisms including humans. Crearley (1973) had reported concentrations of arsenic in surface water near anthropogenic sources such as mining and agrochemical manufactures with range from 0.1 to 10 mg/l. During 1990 to 1997 Chakraborti et.al. (1998) monitored groundwater near insecticide production plant in India and found concentrations of arsenic ranging from 0.05 to 23 mg/l, futher the highest arsenic level was 75 % arsenite.

In Thailand, contamination of domestic water supplies by arsenic causes serious health problem to people living in the Ron Phi bun district, Nakhon Si Thammarat

province. This first recognized in 1987. It was occurred by arsenic spreading from tin ore mining activities over the past 50 years. The arsenopyrite waste from mining had been leached and contaminated shallow wells used by people nearby who become sick and many of them have been infected with skin diseases including alternate pigmentation, small corns on palms and soles, purplish – red flush, and even skin cancer. Those infected people were counted up to 15,000 persons in 1987(Pollution Control Department, 1998).   At present, those mining sites are closed and the arsenopyrite mining wastes were collected by the Department of Mineral Resources to be placed in a secure landfill. However, the construction of the landfill was delayed until 1998. Thus, arsenic was still contaminated in surface water and groundwater, at the total arsenic concentration of 1 mg/l was reported from Ron Phi bun district (Williams, 1996).

There are several methods to remove arsenic from contaminated water including coagulation, precipitation, ion exchange, membrane technology and adsorption. Adsorption process has been shown to be a highly efficient method for removal of colours, odors, organic and inorganic pollutants (Metcalf and Eddy, 1979). Further adsorption technique uses less chemical and this can reduce the cost (Altandogan et al., 2002). The adsorption of arsenic, both As (III) and As(V) in wastewater has also been studied using a variety of materials such as activated carbon , activated alumina and natural materials for example sand, clay, kaolinite, bentonite, montmorrillonite, goethite (Elizalde et al., 2001). Most of removal approach is physical and chemical treatment. However, biological treatment has been studied such as bioremediation.

Diatomite ($SiO_2.nH_2O$) or diatomaceous earth is sedimentary rock composed of microfossil of aquatic unicellular algae commonly known as diatoms. The structure of these diatoms composed mainly of silica. The surface areas of diatomite are silinol group (Si – OH). The unique properties of diatomite are highly porous structure, low density, high surface area and chemical stability. Diatomite is used as a filter aid in beverage industry to help clarify wine, beer and in water purification (Ghouti et al., 2003).   In addition, diatomite has been used as an adsorbent for heavy metals removal

(Khraisheh, Yahya and Wendy, 2003). For this study the modified diatomite by calcination will be used in order to increase its affinity and adsorption capacity. The surface properties of diatomite are modified. The specific surface area and structure are very important factors influencing the adsorption (Ghouti et al., 2003). To increased the surface area of adsorbent , as reported by Jansomboon (2000), Altandogan et al., (2002) and Gonzalez, Einicke and Wennrich, (2001) a thermal procedure are used.

The use of diatomite is cheaper than activated carbon. Further the diatomite is locally available in the country. The use of treated diatomite to the adsorption of arsenic has not yet been studied.

1.1 Objectives

1.1.1 To investigate the possibility of calcined diatomite as an adsorbent for As (III) and As (V).

1.1.2 To investigate the optimum conditions and the efficiency of calcined diatomite adsorbent for As (III) and As (V) from As - spiked water.

1.1.3 To investigate the effects of competing anions on the efficiency of calcined diatomite adsorbent for As (III) and As (V) from As - spiked water.

1.1.4 To study the efficiency of calcined diatomite adsorbent for As (III) and As (V) from arsenic contaminated surface water.

1.2 Scope

This work is focus on As (III) and As (V) removal using diatomite adsorbent by adsorption technique. The diatomite is treated by calcination varied in temperature and time, is supported from Mae Tha district, Lampang province. Two arsenic species As - spiked

water and arsenic contaminated surface water are used in this work. The As - spiked water is prepared in the laboratory and the arsenic contaminated surface water is collected from Ron Phi bun district, Nakhon Si Thammarat province.

1.3 Benefits

1.3.1   To use alternative local, available natural materials used as an adsorbent substitution activated carbon and activated alumina for As – contaminated water treatment.

1.3.2   To find out the optimum condition for As (III) and As (V) removal from contaminated water.

1.3.3   To increase the value of local diatomite for wastewater treatment system.

CHAPTER II

THEORY AND LITERATURE REVIEWS

This chapter gathers the information of the removal of arsenic. The arsenic cycle in environment is discussed and the toxic effects to living organisms are explained in this chapter. Many types of adsorbents using for arsenic removal in wastewater are also given for example.

Theory

2.1 Arsenic

2.1.1 Physical and chemical properties

Arsenic is silver – grey nonmetal or metalloid which is a member of group 15 of the periodic table, with nitrogen, phosphorus, antimony and bismuth. Arsenic has an atomic number of 33 , an atomic mass of 74.9216 ,density of 5.727, melting point at 817 $^{\circ}$C and boiling point at 613 $^{\circ}$C (WHO, 2001). It can exist in four valency states; –3, 0, +3, and +5. Usually it can be found in the form of valency +3 and +5, organic or inorganic arsenic compounds (Sorg and Logsdon, 1978). Organic arsenic compounds are arsenic combined with carbon and oxygen. Inorganic arsenic is generally more harmful than organic arsenic compounds. Under reducing conditions, As (III) may be the dominant form but in oxygenated environments As (V) is the stable oxidation state. Elemental arsenic and arsine (AsH_3) can exist in reducing environments.

2.1.2 Sources

2.1.2.1) Natural Sources

Arsenic is the main constituent of more than 200 mineral species. The most common of the arsenic minerals is arsenopyrite, FeAsS, and also orpiment, (As_2S_3), realgar, (AsS),and enargite,(Cu_3AsS_4) (Azcue and Nriagu, 1994).The concentrations in

the rocks depend on the rock type, and it was found that sedimentary rocks contain much higher concentrations of arsenic than igneous or metamorphic rocks. Concentrations of various types of igneous rocks range from < 1 to 15 mg As/kg (Webster, 1999).

2.1.2.2) Anthropogenic

Arsenic is released into the environment by certain activities of human being, those are:

i) Mining activities

Mining activities can release arsenic in high concentrations from oxidized sulfide minerals .this has resulted in high concentrations of arsenic in surface water, groundwater, soil and vegetation (Azcue and Nriagu, 1994).The stack dust and flue gases from smelters often contaminated soil with arsenic from the operation. There are widely different quantities of anthropogenic ally atmospheric emission, depending upon the industrialization of a country and the degree of pollution control.

ii) Agricultural material

Arsenic has been used and is still used as pesticides and insecticides between 1800s to the mid 1900s. Inorganic arsenicals, usually as lead, calcium, magnesium and zinc arsenate, zinc arsenite or paris green (acetoarsenite) were used extensively as pesticides in orchards. Sodium arsenite was used as a herbicide, while arsenic acid was used as a cotton desiccant. Organic arsenicals were also used as herbicides and desiccants (WHO, 2001) .These used contribute the arsenic – containing compounds discharging into the environment. Hence, arsenic can accumulate in soil, contaminated in both surface and groundwater. It is taken up by plants and is gone into the food chain. Irrigation, especially with wastewaters, can cause a problem of building-up of mobile toxic arsenic in soils and in surface runoff (Siegel, 2002).

iii) Sewage sludge

Arsenic can be found in sewage sludges. The levels of As in the sewage sludges reflect the degree of industrialization of the area served by the sewage system. It is mainly derived from surface run – off bringing in atmospherically deposited As plus residues from pesticide usage. Phosphate detergents add small quantities, and industrial effluents, particularly from the metal processing industry, can add significant quantities.

2.1.3 Uses

Organic arsenic compounds and inorganic arsenic compounds have been used in industry, agriculture and medicine as shown in table 2.1

Table 2.1 Arsenic compounds used in industry, agriculture and medicine (Lenihan and Fletcher, 1977)

Arsenic compound	Formula	Known as	Uses
Arsenic	As		Alloying additive
			Electronic devices. i.e. transistor.etc.
			Veterinary medicines
Arsenic pentaoxide	As_2O_5	Arsenic oxide	Chemical intermediate
			Wood preservative
Arsenic trioxide	As_2O_3	Arsenic	Insecticides and fungicides
		Arsenolite	Glass
		White arsenic	Chemicals
		Arsenious oxide	Timber preservation
Arsine	AsH_3		Stabilizing selenium in transistors

Table 2.1 (Cont.) Arsenic compounds used in industry, agriculture and medicine

Arsenic compound	Formula	Known as	Uses
Calcium arsenate	$Ca_3(AsO_4)_2$		Insecticide, herbicide and larvicide
Potassium arsenate	KH_2AsO_4	Macquer's salt	Textile printing Fly papers
Lead arsenate	$PbHAsO_4$		Insecticide, herbicide.
Sodium arsenate	Na_2HAsO_4	Wolman salts	Wood preservative
Potassium arsenite	$KH(AsO_2)_2$	Fowler's solution	Veterinary medicine
Copper arsenite	$CuHAsO_3$	Paris Green	Larvicide
Sodium arsenite	$NaAsO_2$		Herbicides, Pesticides

Source: Lenihan and Fletcher (1977)

2.1.4 Arsenic in the environment

Arsenic is naturally present in soils and minerals; therefore it may enter in the air, through wind-blown dust and in water through runoff and leaching. As arsenic is associated with ores mined for metal it can comes from mining and smelting. Volcanic eruptions and coal combustion are other ways to release arsenic in the atmosphere. Arsenic may change it form when it enters the atmosphere. Fore example it reacts with oxygen, water or other particles present in the soil or in the air. Arsenic can be attached to big particles that settle on the ground and may be washed out of the air by rain. But arsenic is generally found in small particles that are able to travel long distance during several days (WHO, 2001). Most of these particles are dissolved in water (lake, rivers, underground water). Finally arsenic particles either sediment or ends up in the soil or are carried along by water. The arsenic cycle have been shown in figure 2.1, with the main components of this cycle are air (volatile); mining and smelting; biota (animals, man, plants, and microbes); pesticides and fertilizers; water and oceans; soils, rocks, and sediments; and nonagricultural materials (fossil fuels, industrial and municipal wastes).
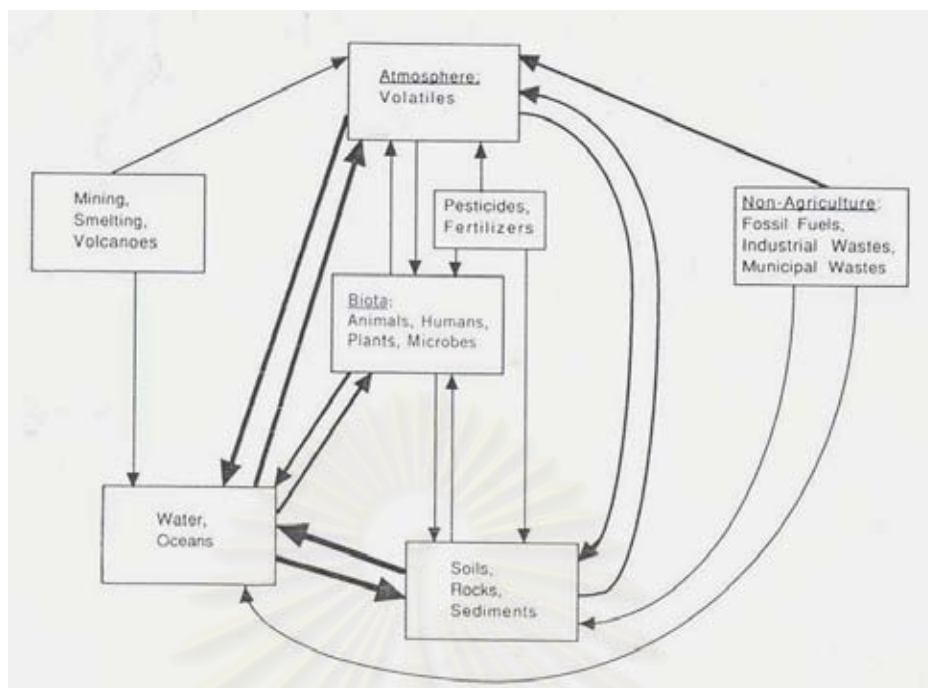
Figure 2.1 A simplified cyclic transfer of arsenic. (Jerome O. Nriagu, 1994)

2.1.5 Arsenic chemistry and the distribution of arsenic in natural water

In natural water, the two major forms are As (III) and As (V). As (III) is found in ground water in nonionic form H_3AsO_3 (pKa $_1$ = 9.20) and anionic form $H_2AsO_3^-$ (pKa $_2$ = 12.13). For As (V) is found in salt acid forms: $H_2AsO_4^-$ (pKa $_1$ = 6.97), $HAsO_4^{2-}$ (pKa $_2$ = 11.53) (Gonzalez, Einicke and Wennrich, 2001. The valence and the species of arsenic are depend on oxidation-reduction conditions and the pH of the water as shown in table 2.2 and the distribution of arsenate and arsenite as a function of pH as shown in figure 2.2.

Table 2.2 The arsenic species and the pH value in natural water (Gupta and Chen, 1978)

pH	As (III)	pH	As (V)
0-9	H_3AsO_3	0-2	H_3AsO_4
10-12	$H_2AsO_3^-$	3-6	$H_2AsO_4^-$
13	$HAsO_3^{2-}$	7-11	$HAsO_4^{2-}$
14	AsO_3^{3-}	12-14	AsO_4^{3-}
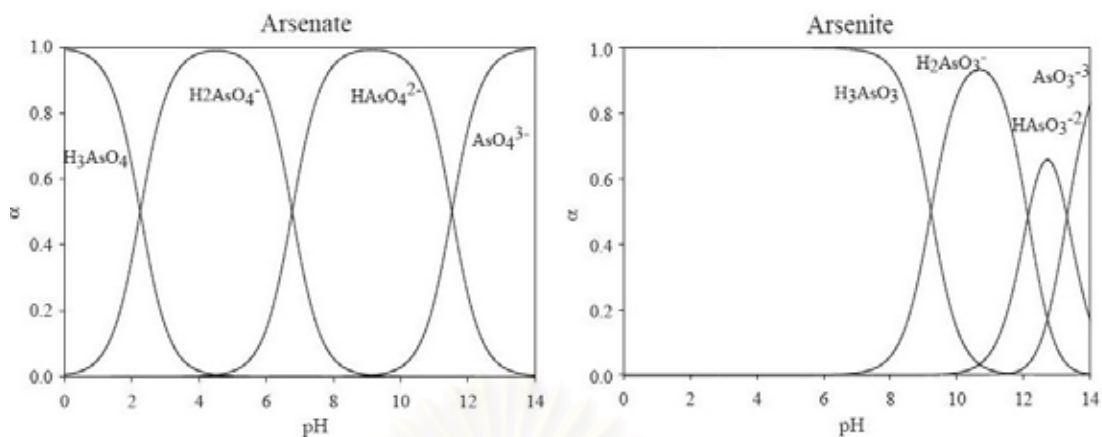
Figure 2.2 Distribution of arsenate and arsenite as a function of pH (Gonzalez, Einicke and Wennrich, 2001)

The distribution of arsenic in natural water

A cycle for arsenic in stratified lake is illustrated in figure 2.3. The reactions include transfers from solution to solid phases, conversions from one oxidation state to another and ligand exchanges. Some of the processes are chemical, some may occur only through microbial remediation, and others may occur either chemically or with microbial remediation.
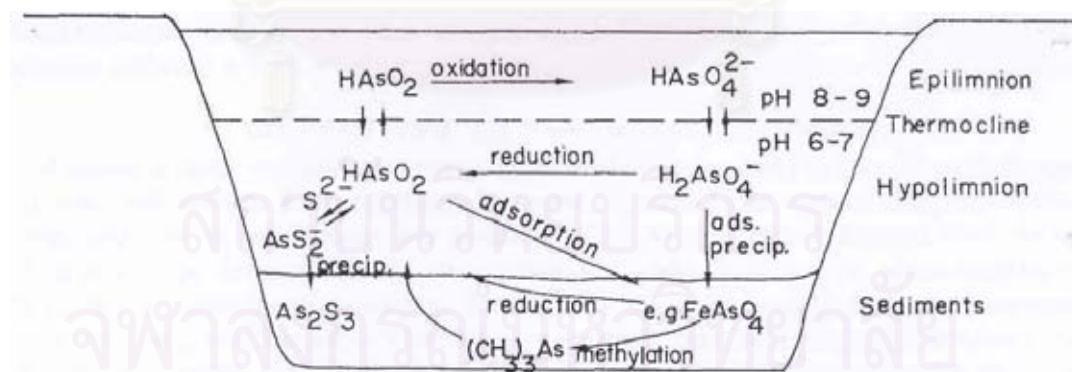
Figure2.3 Local cycle of arsenic in a stratified lake (Ferguson, 1972).

In the aerobic epilimnetic water, reduced forms of arsenic tend to be oxidized to arsenate, which co-precipitates with ferric hydroxide. Turbulent dispersion and convection transport some of the arsenate across the thermocline to the oxygen

depleted hypolimnion, where reduction to $HOAsO_2$ and AsS_2 taking place, depending on the sulfer concentration and the Eh. Coprecipitation, adsorption and epitaxial crystal growth cause arsenic to be removed to the sediment, where reduction of ferric iron, arsenate and arsenite result in either solubilization or stabilization as an insoluble sulfide or arsenic metal. Microbial transmethylation or reduction to arsine solubilize the arsenic and diffusion through the sediments or mixing by currents or burrowing organisms cause the arsenic to re – enter the water column (Ferguson, 1972).

2.1.6 Arsenic toxicity

Arsenic is a highly toxic element and has threatened community health. In general, inorganic arsenic compounds exhibit higher toxicity than organic arsenic compounds. The trivalent species (As (III)) is more toxic than the pentavalent species (As (V)) 5 times, but arsine gas is the most toxic of them all.

As(III) can be toxic through its interation with sulfhydryl groups of proteins and enzymes the proteins and enzymes within the cells and through an increase of reative oxygen species in the cell causing cell damage (Duker, Carranza and Hale, 2004.). As (III) is known to inhibit more than 200 enzymes in the body for example, oxidative stress induced by trivalent methylated arsenials inhibits glutathione (GSH) redutase (Styblo et al., 2000).

As (V) has a similar structure as phosphate as shown in figure 2.3, it can substitute for phosphorus in the body which can lead to replacement of phosphorus in the bone for many years (Ellenhorn and Bareloux, 1988). As (V) is hydrolyzed easily (in the cell), it prevents subsequent transfer of phosphate to adenosine diphosphate (ADP) to form adenosine triphosphate (ATP); (the energy of the cell) and thus depletes the cell of its energy (Winship, 1984) It is also arsenic cause decreases DNA repair process (Brohmoller et al., 2000) and enhances susceptibility to cancer such as skin cancer (Feng et al., 2001).

As (V)   Phosphate

Figure 2.4 The similar of the structure of As (V) and phosphate

The toxicity has shown in two levels, acute toxic and chronic effects.

i)   Acute toxicity

Acute toxicity of arsenic involves many organ systems as shown in table 2.3

Table 2.3 Acute toxicity of arsenic

Organ system	Symptoms and signs	Time of Onset
Gastrointestinal	Burning of mucosae	Immediate
	Nausea and vomiting	Minutes
	Diarrhea with bloody stool	Minutes to hours
Hematologic	Red cell hemolysis	Minutes to hours
	Isolated blood	Several weeks
Pulmonary	Cough	Immediate
Primarily in inhalation	Dyspnea	Minutes to hours
exposures	Chest pain	Minutes to hours
	Pulmonary edema	Minutes to hours

Source: Sullivan and Krieger (1992).

Table 2.3 (Cont.) Acute toxicity of arsenic

Organ system	Symptoms and signs	Time of Onset
Liver	Jaundice	Days
	Fatty degeneration	Days
	Central necrosis	Days
Kidneys	Proteinuria	Hours to days
	Hematuria	Hours to days
	Acute renal failure	Hours to days
Nervous system Central	Confusion / delirium	Hours
	Encephalopathy	Minutes to hours
	Seizures	Minutes to hours
Peripheral	Sensory and motor neuropathy	Several weeks

Source: Sullivan and Krieger (1992).

ii)   **Chronic toxicity**

The most common early signs of chronic arsenic poisoning are small corns or warts, especially on the palms, soles and torso and increased skin pigmentation (darkening) especially of the neck, eyelids, nipples and underarm areas (Winship, 1984). Other signs and symptoms are shown in table 2.4.

Table2.4 Chronic toxicity of arsenic

Target Organ	Effects
Skin/ mucous membranes	Eczema
	Hyperkeratosis, palms and soles
	Warts
	Melanosis
	Mucous membrane irritation
	Squamous cell cancers
Gastrointernal	Stomatitis
	Diarrhea
Hematological	Leukopenia
Kidneys	Anemia
	Pancytopenia
Nervous system Central	Confusion / delirium
	Seizures
Peripheral	Sensory and motor neuropathy

Source: Sullivan and Krieger (1992).

The increasing awarness of the toxicity of arsenic and its carcinogenicity, The WHO guideline value for As in drinking water was provisionally reduced in 1993 from 0.05 mg/l to 0.01 mg/l (WHO, 2001). The new recommended value is based on the ability to measure it quantitatively. The European Union and Japan have drinking water guidelines are also 0.01 mg/l (Ng, Seong and Pierre, 2004). In Thailand, the maximum permissible concentration of arsenic in natural waters by the Pollution Control Department for the protection of human health is 0.05 mg/m^3 and the standard value for control the limit concentration of arsenic for drinking water is 0.05 mg/l as the regard from Ministry of public health as shown in table 2.5.

Table 2.5 The standard values of arsenic contamination from varies sources as follow

	Standard	Source	Standard Values
1.	Bottled Drinking water quality Standards	Notification of Ministry of public health, No. 61, B.E. 2524	Max. Allowable 0.05 mg/l
2.	Industrial Effluent standards	Notification of Ministry of industry, No. 332 B.E. 2521	Max. Allowable 0.05 mg/l
3.	Surface water quality standards	Notification of the national environmental Board, No.8,B.E. 2537	Max. Allowable 0.01mg/l

2.2 Technology for removal arsenic

Because of the strict regulations, water contaminated with As must be treated. There are many processes for removal arsenic, the physical processes, chemical process and biological process.The general processes for arsenic removal have divided in to 6 categories as follows (USEPA, 2000):

2.2.1 Oxidation

As(III) and As(V) are two predominant forms of arsenic in water, most treatment processes are effective for removing As(V), but not As(III), since As(III) is typically non-charged below pH 9.2. Therefore, treatment for the removal of arsenic often includes an oxidation step to convert As (III) to As (V). Oxidation can be simply the addition of oxygen to a compound, or more generally, any reaction involving the loss of electrons from an atom. Aeration, the supplying of air, oxidizes arsenic, converting As (III) to As (V). Arsenic can also be oxidized by a number of other chemicals including chlorine, hypochlorite, ozone, permanganate and hydrogen peroxide. Oxidation process alone does not remove arsenic from solution but must be combined with an other arsenic removal process.

2.2.2 Precipitation/Coprecipitation

Precipitation uses chemicals to transform dissolved contaminants in solution into an insoluble solid with a chemical reaction. Coprecipitation occurs when a contaminant may be dissolved or in a colloidal form. Dissolved contaminants do not precipitate, but are adsorbed form an insoluble complex with the coagulant. Colloidal or suspended contaminants are removed through processes such as coagulation and flocculation. Many processes to remove arsenic from water involve a combination of precipitation and coprecipitation. The precipitated/ coprecipitated solid is removed from the solution by filtration. Arsenic precipitation/coprecipitation can use chemicals such as ferric salts, ammonium sulfate, Alum, maganese sulfate etc.

2.2.3 Ion Exchange

Ion exchange is a physical/chemical process in which ions, held eletrostatically on the surface of the solid, are exchanged for ions of similar charge in a solution. It removes ions from the aqueous phase by the exchange of cations or anions between the contaminants and the exchange medium. Synthetic ion exchange resins are based on a cross-linked polymer matrix typically composed of polystyrene cross-linked with vinylbenzene. Charged functional groups are attached to the matrix through covalent bonding and fall into four groups (Clifford and Lin, 1995 cited in USEPA, 2000) strongly acidic, weakly acidic, strongly basic, and weakly basic. Various strong base anion exchange resins are commercially available that can effectively remove arsenic from water. The categorizing of resins by the type of ion in solution that is the resin preferentially exchanges. For example, resins that preferentially exchange sulfate ions are refer to sulfate-selective resins. Conventional sulfate-selective resins are particularly suited for arsenate removal. Nitrate-selective resins also remove arsenic. Both the redox potential and pH are important factors with regard to arsenic removal by ion exchange.

2.2.4 Adsorption

Adsorption is the accumulation of materials at an interface, the liquid/solid boundary layer. It is a mass transfer process where a substance is transferred from the liquid phase to the surface of a solid and becomes bound by chemical or physical forces. Adsorption can take place on suspended particles, as part of the process of coagulation/co-precipitation, or on fixed media. Since adsorption is a surface phenomenon, the greater the surface area of the medium, the greater it's capacity to accumulate material. Each adsorbent medium has different associated properties, performances and costs. Arsenic is adsorbed onto the surface of various granular, activated, clay and celluosic adsorbents, including: oxides (e.g. hydrated ferric oxide, titanium oxide, and silicium oxide), iron oxide-coated or MnO_2-coated sand, bauxite, hematite, feldspar clay minerals (e.g. kaolinite, bentonite, Bijoypur clay) chitin and chitosan, bone char and cellulose materials (sawdust, newspaper pulp).

2.2.5 Membrane/Reverse Osmosis

Membrane separation uses semi-permeable membranes that are selectively permeable to water and certain solutes to separatecotaminants from water. Membranes are able to remove many different kinds of dissolved solids, including arsenic, from water. However, they are usually expensive and therefore are typically considered in applications such as desalination, brackish water conversion and for removal of specific ions, such as arsenic, that are difficult to remove by other means. There are many different membrane alternatives including microfiltration, reverse osmosis, electrodialysis, ultrafiltration and nanofiltration. Membrane process treatment performance is dependent on the quality of the feed water and the desired quality of the product water. Generally the more contaminated the feed water and the higher the desired product water quality, the greater the likelihood of membrane fouling caused by particulate matter, organic compounds and colloids.

2.2.6 Biological

Biological treatment transforms, stabilizes and/or removes arsenic by means of microorganisms. Microorganisms, primarily certain specific bacteria, accomplish this by oxidation/reduction, mineralization, detoxification or methylation. Critical factors include energy and carbon source; aerobic, anoxic or anaerobic conditions; temperature; pH.

2.3 Adsorption principles

2.3.1   Definition of adsorption terms

Adsorption is a surface phenomenon that is defined as the increase in concentration of particular compound at the surface of interface between solid or liquid phase. Adsorbent is the phase that collects the substance to be removed at its surface. Adsorbate is the solute that is to be adsorbed and isotherm is a relation between the equilibrium amount of a substance adsorbed per weight of sorbent and its concentration in the liquid at the constant temperature. In discussing two fundaments of adsorption, it is useful to distinguish between physical adsorption, involving only relatively weak intermolecular force and chemisorption, which involves essentially the formation a chemical bond between the sorbate molecule and the surface adsorbent (Noble and Terry, 2004). Physical adsorption can be distinguished from chemisorption according to one or more the following criteria.

Table.2.6 Different of physical and chemical adsorption (Noble and Terry, 2004)

Parameter	Physical adsorption	Chemical adsorption
Force	Van Der Waals	Covalent bond
Reversibility	Reversible	Irreversible
Specific site	Non specific	More specific
Layer on the surface	Multiple sorbate layers	Monolayer
Heat of adsorption	Low	High
Energy	Low	High (20 - 100Kcal/mol)

2.3.2 Mechanism of adsorption

Sorption process is defined as the selective transfer of solute from the bulk solution onto the surface of the adsorbent. The solute transfer process is assumed to proceed through the following four mechanisms :(Metcalf and Eddy, 1979).

1. Transfer of solute (adsorbate) from the bulk solution onto the surface film (boundary layer) which surrounds the adsorbent particle. This step is controlled by convective flow and turbulent mixing.

2. Transfer of the adsorbate across the surface film to the exterior surface of the adsorbent particle. This step is controlled by molecular diffusion.

3. Transfer of the adsorbate from the relatively small area of external particle surface to the pores within the pores of each adsorbent particle. Majority of adsorption occurs in the pores, because of the more availability of surface area (m^2 / g). This step can be accomplished in two ways: pore diffusion (diffusion through the fluid in the pore); and surface diffusion (the particle moves along the pore surface)

4. Physical or chemical binding of the adsorbate to the internal surface of the adsorbent. The molecules of adsorbate adhere to the surface in the pore and finally adsorbate transfer process terminates after equilibrium.This step is controllrd by the molecular interactions.
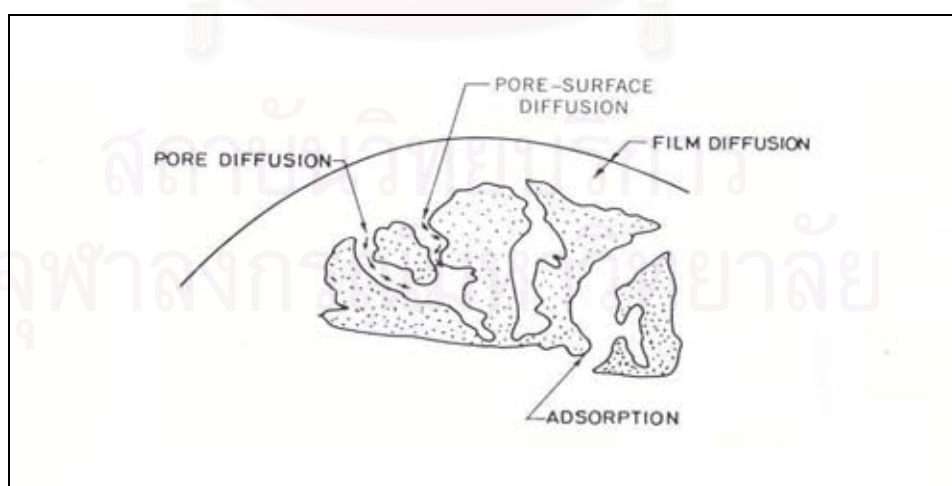
Figure 2.5 The particle transport during adsorption by microporous solids (Metcalf and Eddy, 1979)

2.3.3 Equilibrium sorption isotherm

The equilibrium isotherms are very important in designing adsorption systems. To estimate the adsorption characteristics of an adsorbent. Generally both Langmuir and Freundlich isotherms are used for explaining the adsorption of metal ion Langmuir and Freundlich equations are given below.

i) Langmuir Adsorption Isotherm

$$Ce/(X/m) = 1/(bqm) + Ce/qm \qquad (1)$$

Where X is the amount of adsorbate absorbed, m is the amount of adsorbent, Ce is the equilibrium concentration of the adsorbate in the solution and b is a constant that represents adsorption bond energy and qm a constant that represents maximum adsorption density corresponding to a monolayer covering the surface of the adsorbent. Eq. (1) is also sometimes written as,

$$1/q = [1/(bq_m) \times (1/Ce)] + [1/q_m] \qquad (2)$$

Where Ce and q were equilibrium solute concentration (mg/l) and equilibrium adsorption capacity, respectively (mg/g), qm and b the Langmuir constants representing adsorption capacity (mg/g) and energy of adsorption (L/mg), respectively. The value of qm and b were calculated from the slope and intercept of the linear plot of (1/qe) versus (1/Ce) should yield a straight line as shown in figure 2.6 .
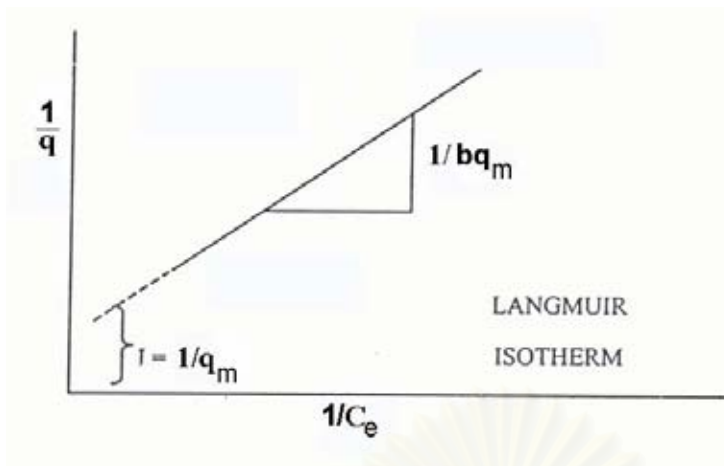
Figure 2.6 Langmuir Isotherm

ii)Freundlich Adsorption Isotherm

$$X/m = kCe^{1/n} \tag{3}$$

Where X, m and Ce have the same meaning as described in Langmuir isotherm .
k is constant. taking the logarithm of Eq. (3)

$$\text{Log} (X/m) = \text{Log} k + 1/n \text{ Log } Ce. \tag{4}$$

If the adsorption data follow Freundlich pattern plot of log (X/m) with log Ce should
yield a straight line and n and k may be calculated from the slope and intercept,
respectively.
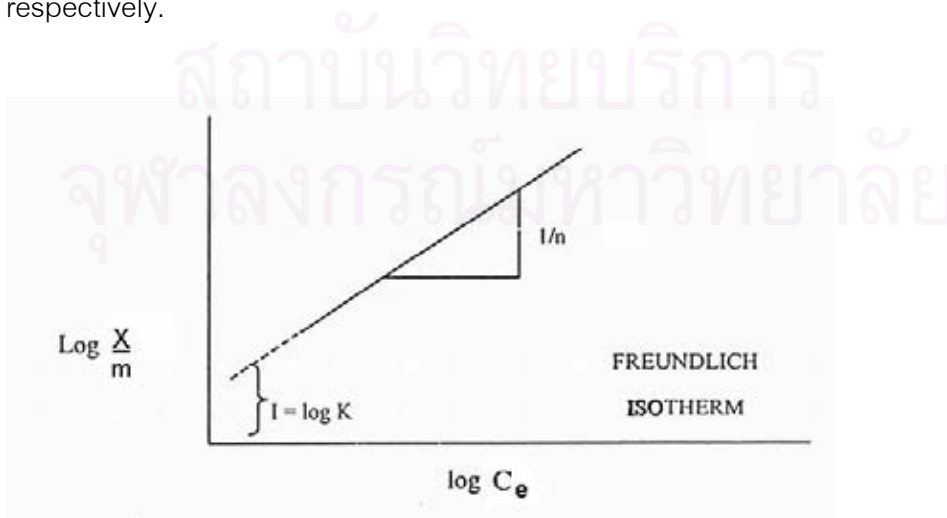
Figure 2.7 Freundlich Isotherm

2.4 Diatomite or diatomaceous earth

Diatomite refers to sedimentary rocks that are mainly composed of the skeleton of single – celled diatoms. Diatoms can be occurred in marine, branckish, and fresh water environments. Diatomite consists of a wide variety of shape and sized diatoms, typically 10 - 200μm, in a structure containing up to 80 – 90 % voids (Ghouti et al., 2003). The skeletons are composed of opal – like, amorphous silica ($SiO_2.xH_2O$) and exhibit a wide range of porous fine structures and shapes. Diatomite is lightweight and highly porous. It has a large surface area of 50 – 200 m^2/g (Yang et al., 2003). Their properties are low density, high porosity, high absorption capacity for liquids and low thermal conductivity (Uhllman, 2003). As a result of its unique physical and chemical properties, diatomite has been put in industrial utilization as filtration media for various beverages. In addition, there were hydrogen bonded hydroxyl groups on the surface of diatomite. It can be performed to used as an adsorbent for removing heavy metal ions, for example Pb^{2+} , Cu^{2+} and Cd^{2+} (Khraisheh, Yahya and Wendy, 2003), textile dyes (Ghouti et al., 2003). The chemical composition of diatomite is shown in table 2.6

Table 2.7 The chemical composition of various diatomites

Diatomite	Chemical composition, %					Loss on ignition
	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	
Inzensk (Russia)*	82.66	4.55	3.21	1.23	0.47	4.78
Kisatibi (Georgia)*	94.14	1.98	0.28	0.17	0.85	2.93
Gurmen (Bulgaria)*	68.80	13.70	5.30	0.90	1.10	-
Batkovistsy (Bulgaria)*	81.80	9.40	2.90	1.00	1.20	3.80
Lompoc (USA)*	89.30	4.00	0.70	0.40	0.40	5.00
Ma Tha (Thailand)**	72.50	11.50	3.85	1.12	2.10	-

* Dabrowski (1999)

** Kumanchan and Triyan (1994)

Uses

The main uses of diatomite are the following: 60% of world production is used as a filtration agent; 25% as filler diatomites, including carrier materials; and 15% for other uses (Uhllmann, 2003).

Filtration Agents. Diatomite is used in both pressure and vacuum filters of various designs:fine, medium, and coarse diatomites,coarse diatomites are used for precoat filtration in pressure filters in amounts of 1 kg/m2 of filter area. Fine and medium diatomites are added to the slurry to be filtered, usually in amounts of 10 – 200 g/m2 filter area.The most important uses of diatomite are the filtration of beer, wine, fruit juice, sugar cane juice, swimming pool water, solvents for chemical cleaning, wastewater, varnishes, and paints etc.

Fillers. Diatomite is used as filler and auxiliary. For example, to modify the rheological properties of polymers. It increases the thermal stability of bitumen, the Shore A hardness of silicone rubber, and is a reinforcing filler in plastics, rubber, and adhesives. Activated diatomite is used as a delustering agent, for adjusting the viscosity of paints, and as an antiblocking agent for plastic films.

Insulators. Loose diatomite has long been used for insulating double – walled kilns made from fireclay bricks, as well as for producing insulating sheets and bricks. Danish Moler is especially well suited for producing insulating bricks, since its clay content functions as a ceramic binder. In the VSI process (vacuum super insulation), a special form of diatomite acts as a supporting and insulating layer in double – walled elements that containa high vacuum. Thus, extremely high insulation values are achieved. The VSI process is being tested for long – distance heat transport.

Absorption Agents. Due to their high capacity for liquids, diatomites are used to produce gas purification agents as well as absorption agents such as cat litter and

drying agents.Diatomite is also used to ensure the flowability and to prevent clotting of food stuffs, fire extinguisher powders, and seeds.

Other Uses. Diatomite serves as a fine scourer in polishes and cleaners such as car polishes, toothpastes,and silver polishes. Diatomite is employed as a catalyst support, for the production of pyrotechnics and matches, as a packing material for the transportation of hazardous liquids, and for the filling of acetylene bottles. In some countries it is used as the silica source for the production of cement and calcium silicate.

2.5 Diatomite Processing

There are 3 types of processed diatomite: Dried diatomite, Calcined diatomite and Flux- calcined diatomite. In order to retained the most important property of diatomite as the high porosity. The processing method for diatomite should be minimized damage to the structure of the diatomite the sintering during calcinations should not be destroyed the form and not blocked the pores of diatomite. (Uhllmann, 2003).

i) Dried Diatomite

The diatomite from the deposits site contains 30-65% water, depending on the climatic conditions at the production site, is removed in counter current driers, Drying is practiced to classify the diatomite product with a low moisture content. After drying it is fallowed by gentle grinding and screening to give product, that are used as absorbents such as for oil or as pet litter. However, Apart from this if the raw diatomite is of high purity and has low content of organic substances, that dried diatomite can be used as filtration agent also.

ii)   Calcined Diatomite

Calcination is the process of heating a substance to a high temperature, but below its melting or fusing point, to bring about thermal decomposition or a phase transition in its physical or chemical constitution.

The furnace is used to calcine diatomite because it has the advantage of a slow calcinations process at relatively low temperature which causes little damage to the structure. Calcination is the types of processed diatomite to remove organic substances and after the particle size, dried diatomite is calcined in furnace at 800 – 1000 $^\circ$C. During calcinations, the diatom frustules and their fragments are hardened and partially agglomerated by sintering. The degree of sintering, relative to the pore porosity, can be controlled by altering the temperature and duration of the process. After calcinations the diatomite is ground and classified into grades with different particle size (fine and medium) calcined diatomite. The content of water and organic substances can be removed by calcination. Higher iron contents can be refined by calcinations. Iron impurities, present as Fe_2O_3 after calcinations (ref. พรรณิภา / รวม journal), This diatomite vary in colour from yellowish to pink or dark brown, depending on their origin, and iron impurities presented as Fe_2O_3 after calcinations. Fine and medium diatomites are used as filter aid in many industries field.

iii)   Flux – Calcined Diatomite

In this process, dried or calcined diatomite is calcined with the addition of alkaline fluxes. Sodium Carbonate is used as flux in amount of 1 – 6 %, the calcinations temperature is 1000 - 1200°C. The additions of flux lead to the formation of a sodium silicate glass melt which binds the diatom frustules and their fragments into agglomerates. Since the iron contained in the diatomite is also bound, a while product is

formed. The degree of agglomeration is depending on the temperature variation, type and amount of flux and the reaction time. This process is known as activation.

The high calcinations temperatures in the presence of alkaline lead to a partial transformation (up to 65%) of the amorphous silica into cristobalite, a crystalline silica modification. The porosity and the specific surface area are strangely decreased. The grinding and classification processes are followed to give white filter diatomite (the main product) and a dust like fine fraction which is used as filler and auxiliary.

The quality criteria of diatomite for various applications as filtration agents choose calcination diatomite because the important quality criteria for diatomite including the particle-size distribution, shape and fine structure of the diatoms can be altered with regard to their structural framework and porosity by calcinations). In addition, the chemical and mineralogical composition of calcined diatomite has important, since higher contents of components can limit economically viable processing and refinement of diatomite. The physical tests and chemical analysis of calcined diatomite are shown in Table 2.7.

Table 2.8 Chemical and physical properties of commercially available diatomite's (Uhllmann, 2003)

Properties	1	2	3	4	5	6
Colour	White-gray	Yellow-brown	Pink	White	White	yellow-brown
SiO_2, %	89.0	87.5	90.7	89.5	90.7	90.2
Al_2O_3, %	3.5	4.3	3.9	4.1	3.9	2.8
Fe_2O_3, %	0.9	2.9	1.4	1.6	2.1	2.5
CaO, %	1.1	1.9	0.5	0.5	1.0	0.7
Na_2O,K_2O, %	0.8	0.8	0.9	3.6	3.5	0.9
Ignition loss, %	2.0	0.7	0.5	0.2	0.1	0.4

Table 2.8(cont.) Chemical and physical properties of commercially available diatomite's (Uhllmann, 2003)

Properties	1	2	3	4	5	6
Bulk density, g/L	107	140	120	229	200	209
pH Value	7.0	6.9	7.5	10.0	9.7	6.7
Water uptake, %	255	205	250	156	160	196
Specific surface area,m^2/g	19.2	13.0	15.2	1.9	1.6	10.6
Average particle size, μm	14.2	14.1	15.9	22.5	30.1	14.7
Wet density, g/L	228	255	271	297	290	357
Permeability, Darcy	0.06	0.09	0.28	1.20	1.60	0.08
Crystalline content, %	2.0	9.2	7.6	58.1	59.7	10.3

*1) American filter diatomite, dried; 2) French filter diatomite, calcined; 3) American filter diatomite, calcined; 4) American filter diatomite, flux calcined; 5) French filter diatomite, flux calcined; 6) German regeneration filter diatomite, calcined.

2.6 Literature reviews

Arsenic removal by various adsorbents

In water treatment, an adsorption processes have been shown to be highly efficient for removal of colours, odours, organic and inorganic pollutants (Elizalde et al., 2001). For the removal of arsenic adsorption processes are diversified according to adsorbents used. Conventional adsorbents such as activated carbon (AC) (Gupta and Chen, 1978) and activated alumina (Singh. and Pant., 2003) have been used. Natural adsorbents for example, red clay (Junsomboon, 2000), hematite (Altandogan et al., 2002, Zhang et al., 2004), goetite (Ladeira and Ciminelli, 2003) zeolite (Shevade and Ford, 2004) were investigated. Uses of naturally occurring ores and minerals such as manganese ore (Chakravarty et al., 2002) and natural iron ores (Zhange et al., 2003) have been reported. Table 2.8 showed examples of some adsorbents have different optimum conditions for the efficiency of removal As (III) and As (V) by adsorption.

Regarding for safe and economic factors, natural adsorbents were the most widely used adsorbents for a large number of different compounds. They were contained mineral materials with oxide surface especially iron oxides. Altandogan et al (2002) have been reported that the adsorption of arsenic on iron has a strong nature and the precipitation – coagulation with ferric salts is used as conventional method for arsenic removal from aqueous systems.

However, the adsorption capacity of As (III) by natural adsorbent should be improved. Zhange et al (2003) studied the removal of As (III) by natural hematite and found the maximum capacity was only 0.2 mg/g As (III). They also reported that As (III) was removal to some extent, and that natural oxides can be applied for adsorption. The problem may be the small specific surface area of natural oxides.

Table2.8 (cont.) Arsenic removal by adsorption

Adsorbent	As Concentration (mg/l)	Efficiencies	Optimum pH	References*
AC	1.90	As(V) removal : 92.4%	3.1	1
AC(char carbon)	1	As(V)loading:34mg/g	3	2
Activated Alumina	0.5	As(III) removal: 96.2%	7.6	3
Red clay	10	As(III) removal: 84 %	4	4
		As(V) removal : 100%	4	4

Table2.8 (cont.) Arsenic removal by adsorption

Adsorbent	As Concentration (mg/l)	Efficiencies	Optimum pH	References*
Hematite	10	As(III) removal: 88%	3.5	5
		As(V) removal : 97%	7.25	5
Goethite	10	As(III) removal: 75%	5.5	6
		As(V) removal : 90%	5.5	6
Zeolite	50	As(V) removal : 90%	7.5	7
Manganese ore	1	As(III) removal: 100%	4 - 8	8
	1	As(V) removal : 100%	4 - 8	8
Natural iron ores	1	As(V) removal : 100%	4.5 – 6.5	9

* References: 1. Gupta and chen (1978) 2. Pattanayak et al.(1999) 3. Singh (2003) 4. Junsomboon (2000) 5. Altandogan et al. (2002) 6. Ladeira and Ciminelli (2003) 7. Shevade and Ford (2004) 8. Chakravarty et al.(2002) 9. Zhang et al. (2004)

Besides, using various different adsorbents are affected to arsenic removal, there are many factors are affected also for example as followed:

i) The pretreatment of adsorbents

ii) The factor affecting arsenic adsorption performance such as pH, Contact time Concentration

iii) The presence of others ionic in the aqueous solution.

i) The pretreatment of adsorbents

The pretreatment techniques are used to improve quality and capacities of adsorbents for removal arsenic from water and wastewater. Some adsorbent such as activated carbon is activated by heating and / or chemical treatment. Saejen (2000) studied Coconut shell:FeCl$_3$ (1:3) adsorbent which prepared by chemical activated process for removal As(III) and As(V). She found that the adsorption capacity for As(III) and As(V) were 0.03 and 3.26 mg As/ g activated carbon. Heated activated carbons are found to be more effective for arsenic adsorption (Pattanayak et al., 1999). Pretreatment the zeolite (Elizalde et al., 2001) and red mud (Altundogan et al., 2002) by calcination also shown significant improvement in arsenic removal . Tarasevich (1998) reported that in the filler industry the natural diatomite is calcinated at a temperature 1000 $^{\circ}$C to produce the most effective filtration powders. After calcination, he found that small – size pores disappear due to sintering and the radius of macrospores and their number in the structure of amorphous silica increase. In Thailand natural adsorbent such as activated red mud could remove arsenic by heating and treating with acid (Junsomboon, 2000).

Chemical pretreatment method has been used on adsorbent to improve the adsorption capability. Wu, Yang and Lin (2005) used the raw and modified diatomite for advanced treatment of secondary sewage effluents (SSE). They found that 30 % of arsenic was removed at pH 6.12 and dosing rate of 300 mg/L. Therefore, raw diatomite could be improved by using chemically – modified diatomite. The chemically – modified diatomite was prepared by mix raw diatomite powder with solid aluminum sulfate and lime at the ratio of 6:1:3, the mixed sample was treated in an ultrasonic bath for 15 min and then oven drying at 60°C. The dried samples were ground through a 100 – mesh sieve, and charred in muffle furnace at temperature of 450°C for 2 h. After treatment of SSE with modified diatomite they found that the removal efficiency of arsenic was improved to 60% at pH 7.62 and dosing rate of 300 mg/L. This indicated that the modified diatomite performed better than raw diatomite in the SSE wastewater treatment.

Heat treatment and acid treatment methods have been tested on many adsorbents to increase arsenic adsorption capability. Altandogan et al. (2002) studied arsenic adsorption by raw and activated red mud. Two methods were used to activate the red mud. In the first method, the red mud was heat-treated at various temperature (200, 400, 600 and 800 $^{\circ}$C) for 4 hours. In the second method, red mud was activated through acid treatment by using 0.25 – 2.0 M HCl solutions. They found that the adsorption capacity of red mud was increased by acid treatment with 1M HCl solution. The maximum arsenic removals were 96.52% for As (V) and 87.54% for As (III) in the solution with arsenic concentration of 10 mg/l with a final pH of 7.25 and 3.50 respectively, contact time 60 min and activated red mud dosage of 20 g/L.

ii) The factor affecting arsenic adsorption performance

The adsorption of As(III) and As(V) onto some natural materials, generally encountered in soil – water systems, with special emphasis on the role of process variables such as concentration, pH of the system, and contact time. Table 2.9 – table 2.11 are shown the controlling factors for the removal of arsenic.

Effect of pH

Table 2.9 Some examples indicating the effects of pH

Adsorbent	Effects
Red mud (Altandogan et al., 2002)	Increasing adsorption rate of As(V) and As(III) with increasing pH
Goethite (Lenoble et al., 2002)	No effects of pH on As(III) and As(V) adsorption
Goethite (Ladeira and Cimineli, 2003)	Increasing adsorption rate of As(V) and As(III) with decreasing pH
Zeolite (Shevade and ford, 2004)	Decreasing adsorption rate of As(III) and As(V) with increasing pH
Iron based cerium ions(Zhange, Yang and Huang, 2003)	Increasing adsorption rate of As(V) with decreasing pH

Effect of concentration

Table 2.10 Effect of concentration on adsorption

Adsorbent	Effects
Goethite (Lenoble, 2002)	As(III) and As(V) removal increased as the concentration increased from 0 to 30 mg/L

Effect of contact time

Table2.11 Effect of contact time on adsorption

Adsorbent	Effects
Red mud (Altandogan et al., 2002)	As (V) removal increased with time in the ranging of time 30 to 270 min.
Silica – containing iron (III) oxide adsorbent (Zeng, 2003)	Aging times from 1 to 7 days are not significant effect on the arsenic adsorption.

iii) The presence of other ionics in the aqueous solution

Competition for adsorption sites could reduce the effectiveness of adsorption because other constituents may be preferentially adsorbed. Several studies have illustrated the presence of other anionic components such as sulphate, phosphate, chloride or natural organic matters are reportedly affected the adsorption capacity of arsenic. The effect of ions on adsorption are showed in Table 2.12.

Table2.12 Effect of ions on adsorption

Adsorbent	Effects
Iron hydroxide (Korfiatis et al, 2002)	As(III) removal is reduced in the presence of phosphate and silicate
Ferric chloride (Meng et al, 2003)	Sulfates and Carbonate are affected on As (III) and As (V) removal.
Aluminum – loaded zeolite (Xu et al, 2002)	The addition of chloride, nitrate and acetate ions are affected the As(V) adsorption The existing of phosphate and sulfate could reduced the removal of As(V)
Pillared clays (Benjamin et al., 1998)	Increasing sulfate from 0 to 100 mg/L has only a small impact on the sorption of As(V) The presence of chloride did not affect As (V) removal.

CHAPTER III

EXPERIMENTAL

There are four sections of the experiment described in this chapter. The first section described the scope of the experiment. The chemical reagents, adsorbent material and experimental apparatus were described in the second section. The third section described the experimental procedures and the experimental calculation was described in the last section.

3.1   The scope of the experiment

3.1.1   Investigated the efficiency of diatomite and calcined diatomite in removal As (III) and As (V) in As - spiked water.

3.1.2   Determined physical and chemical properties of diatomite and calcined diatomites.

3.1.3   Investigated the optimum condition of As (III) and As (V) removal in As - spiked water using calcined diatomite by vary concentration of As(III) and As(V), pH, the contact time and the amount of adsorbent.

3.1.4   Investigated the effects of competing ions on As (III) and As (V) removal in As - spiked water.

3.1.5   Investigated the efficiency of diatomite adsorbent in removal As in arsenic contaminated surface water from Ron Pibun Nakorn Sri Tammarat province.

3.2   Chemical reagents, adsorbent material and apparatus

3.2.1   Chemical reagents

Number	Reagent	Reagent Type
1	Sodium arsenite(NaAsO$_2$)	Analytical Reagent Grade
2	Arsenic Acid (H$_3$AsO$_4$)	Standard solution Analytical Reagent Grade
3	Nitric acid 65% (HNO$_3$)	Analytical Reagent Grade
4	Hydrochloric acid 37 %(HCl)	Analytical Reagent Grade
5	Sodium hydroxide(NaOH)	Analytical Reagent Grade
6	Sodium chloride(NaCl)	Analytical Reagent Grade
7	Potassium nitrate(KNO$_3$)	Analytical Reagent Grade
8	Potassium dihydrogenphosphate (KH$_2$PO$_4$)	Analytical Reagent Grade
9	Sodiumbicarbonate (NaHCO$_3$)	Analytical Reagent Grade

3.2.2   Adsorbent Material

Diatomite used in this work was kindly provided from Ma tha district, Lampang province.

Apparatus

Number	Apparatus	Brand : series
1	Weigh Balance 4 digits	Mettler : AB204 - S
2	Weigh Balance 2 digits	Mettler : PB3002 - S
3	Furnace	Carbolite : RHF 1600
4	Shaker	GFL : 3015

Number	Apparatus	Brand : series
5	pH Meter	Denver instrument :Model 215
6	Inductively Coupled Plasma Atomic Emission Spectroscopy	Perkin-Elmer :Plasma - 1000
7	Scanning Electron Microscope	JSM :6400
8	X-ray Fluorescent	Phillip: PW 2400
9	Bet Surface Area Analyzer	FlowSorb: 2300
10	Oven	Memmert: 500
11	Microwave Digester	Cem: Mars 5
12	Sieve	Endecotts: S/STEEL
13	Filter Paper No. 42	Whatman
14	Aluminum foil	Diamond
15	Glass wares	

3.3 Experimental Procedure

In this work, there were 3 variables including fixed varibles, Independent variables and dependent variables as shown in table 3.1, 3.2 and 3.3 respectively.

Table 3.1 Fixed variables and parameter

Number	Fixed variables	Parameter
1	Speed of shaker	180 rpm
2	Temperature of experiment	room temperature (25 -28 $^{\circ}$C)
3	Volume of As - spiked water	50 ml
4	Particle size of diatomite	100 mesh

Table 3.2 Independent variables and parameters.

Number	Independent variables	Parameters
1	Calcination temperature	200, 400, 600, and 800 $^\circ$C
2	Calcination time	2, 4, 6, and 8 hours.
3	Concentration of As(III)and As(V)	0, 0.5, 1.0, 2.0, 5.0 and 10.0 mg /L
4	pH	4, 5, 6, 7, 8, and 9
5	Contact time	30, 60, 120, 180, 240, 300, 360 and 420 minutes
6	Amount of diatomite	0.1, 0.5, 1.0, 2.0, 3.0 and 4.0 g
7	Concentration of anions :Cl^-, NO_3^-, PO_4^{3-} and CO_3^{2-}	0, 10, 100, 500 and 1000 mg/l

Table 3.3 Dependent variables

Number	Dependent variables	Parameters
1.	As - spiked water after experiment	Remained concentration pH value of solution after experiment
2.	Effective removal	Percentage of As(III) and As(V) removal

3.3.1 Experimental Preparation

3.3.1.1 Preparation of Glasswares

Before all glasswares were used in this work. They were immersed in 10% HNO_3 overnight. After they were washed with clean water , rinsed 3 times

with deionized water to ensured that there was no acid deposited inside and dried in 80 $^{\circ}$C oven.

3.3.1.2 Preparation of Arsenite solution (Shraim et al., 2001)

Dissolved 1.7340 g NaAsO$_2$ in deionized water and diluted to 1000 ml as an arsenite stock solution contained 1000 mg As(III) /l. Pipette 25 ml of the stock solution and diluted with deionized water to 250 ml as an arsenite standard solution contained 100 mg As(III) /l . The arsenite standard solution contained 100 mg As (III) /l was diluted with deionized water to desired concentration as shown in table 3.2. An arsenite stock solution and an arsenite standard solution were stored in refrigerator at 4 $^{\circ}$C.

3.3.1.3 Preparation of Arsenate solution (Santosa, 2001)

Pipette 25 ml of 1000 mg/l arsenous acid stock solution and diluted with deionized water to 250 ml as an arsenate standard solution contained 100mg As (V) /l. The arsenate standard solution was diluted with deionized water to desired concentration as shown in table 3.2. An arsenate stock solution and an arsenate standard solution were stored in refrigerator at 4 $^{\circ}$C.

3.3.1.4 Preparation of diatomite adsorbent

The diatomite was washed with distilled water to remove fines and other adhered impurites, dried at 80 $^{\circ}$C for 24 hours, descicated and sieve through 100 mesh sieve. The sample was kept in polyethylene zip lock bag at temperature room in desiccators until it was used.

3.3.1.5 Preparation of diatomite calcination adsorbent

50 g of diatomite with no sieve from 3.3.1.4 was weighed in. It was calcined at various temperature 200, 400, 600 and 800 $^{\circ}$C for 2, 4, 6 and 8 hours in furnace. The rate of calcination was 2 $^{\circ}$C/min. At the end of the calcination, sample was kept in polyethylene zip lock bag at temperature room in desiccators until it was used. In this work, the calcined diatomite (CD xy) is used. In this work, the calcined diatomite (CD xy) is referred to the diatomite calcination at various temperature(x) and time (y). For example CD2002 is referred to as the diatomite calcination at 200 $^{\circ}$C for 2 hours.

3.3.1.6 Preparation of chloride standard solution 1000 mg/l

1.6480 g sodium chloride (dried for 2 hours at 105 $^{\circ}$C) was dissolved and made up to 1 L with deionized water.1 ml of this solution contained 1 mg chloride.

3.3.1.7 Preparation of nitrate standard solution 1000 mg/l

1.6307 g potassium nitrate (dried for 2 hours at 105 $^{\circ}$C) was dissolved and made up to 1 L with deionized water.1 ml of this solution contained 1 mg nitrate.

3.3.1.8 Preparation of phosphate standard solution 1000 mg/l

4.3937 g potassium dihydrogenphosphate (dried for 2 hours at 105 $^{\circ}$C) was dissolved and made up to 1 L with deionized water.1 ml of this solution contained 1 mg phosphate.

3.3.1.9 Preparation of carbonate standard solution 1000 mg/l

1.3999 g sodium bicarbonate (dried for 2 hours at 105 $^{\circ}$C) was dissolved and made up to 1 L with deionized water.1 ml of this solution contained 1 mg carbonate.

3.3.2 The investigation of the efficiency of diatomite and calcined diatomite in removal As(III) and As(V) in arsenic- spiked water

3.3.2.1 The investigation of the efficiency of diatomite and calcined diatomite in removal As (III) in arsenic- spiked water

All samples of diatomite and calcined diatomites from 3.3.1.4 and 3.3.1.5 were used in this study. 50 ml of 10 mg/l As (III) solution was taken into 125 ml Erlenmeyer flask. pH of the solution was adjusted pH to 7 by using 1 N sodium hydroxide. The 0.5 g of sample was added in the flask, covered with aluminum foil and was shaken at 180 rpm for 2 hrs, each experiment was duplicated and the blank solution was used as a control. The solution was immediately filtered through filter paper. The filtrate was determined for the concentration of arsenic by ICP-AES.

3.3.2.2 The investigation of the efficiency of diatomite and calcined diatomite in removal As (V) in arsenic- spiked water

All samples of diatomite and calcined diatomites from 3.3.1.4 and 3.3.1.5 were used in this study. 50 ml of 10 mg/l As (V) solution was used and repeated 3.3.3.1.

3.3.3   Determination Physical and Chemical Properties of the diatomite and calcined diatomite

The diatomite from 3.3.1.4 and the calcined diatomite which had high As (III) and As (V) removal efficiency from 3.3.2.1 and 3.3.2.2 were determined physical and chemical properties by Bet Surface Area Analyzer, X- ray fluorescent. In order to selected the best diatomite adsorbents to use in the next experiment.

3.3.4   The investigation of the optimum conditions of As (III) and As (V) removal in As - spiked water

4 conditions as shown in table 3.2 were investigated; concentration, pH, contact time and amount of the diatomite.

3.3.4.1 Concentration of adsorption

The As (III) and As (V) solutions were prepared by varying the concentration from 0.5, 1, 2, 5 and 10 mg/l. A 50 ml of each arsenic solution was taken into 125 ml Erlenmeyer flask and   adjusted pH to 7 by using 1 N sodium hydroxide. 0.5 g of diatomite from 3.3.3 was added in each flask, covered with aluminum foil and was shaken at 180 rpm for 2 hrs. Each experiment was duplicated and the blank solution used as control. The solution was immediately filtered through filter paper. The filtrate was determined for the concentration of arsenic by ICP-AES.

3.3.4.2 pH of adsorption

The As (III) and As (V) solutions were prepared by using the optimum concentration in 3.3.4.1. A 50 ml of each arsenic solution was taken into 125 ml Erlenmeyer flask and   adjusted pH to 4, 5, 6, 7, 8 and 9 by using 1 N nitric acid

or 1 N sodium hydroxide.0.5 g of diatomite from 3.3.3 was added in each flask, covered with aluminum foil and was shaken at 180 rpm for 2 hrs. Each experiment was duplicated and the blank solution used as control. The solution was immediately filtered through filter paper. The filtrate was determined for the concentration of arsenic by ICP-AES.

3.3.4.3 Contact time of adsorption

The As (III) and As (V) solutions were prepared by using the optimum concentration in 3.3.4.1. A 50 ml of each arsenic solution was taken into 125 ml Erlenmeyer flask and   adjusted pH to the optimum pH in 3.3.4.2 by using 1 N nitric acid or 1 N sodium hydroxide.0.5 g of diatomite from 3.3.3 was added in each flask, covered with aluminum foil and was shaken at 180 rpm the contact time was varied from 30, 60, 90, 120, 150, 180, 240, 300, 360, and 420 minutes. Each experiment was duplicated and the blank solution used as control. The solution was immediately filtered through filter paper.   The filtrate was determined for the concentration of arsenic by ICP-AES.

3.3.4.4 Amount of the optimum diatomite

The As (III) and As (V) solutions were prepared by using the optimum concentration in 3.3.4.1. A 50 ml of each arsenic solution was taken into 125 ml Erlenmeyer flask and   adjusted pH to the optimum pH in 3.3.4.2 by using 1 N nitric acid or 1 N sodium hydroxide. The diatomite adsorbent from 3.3.3 at various weights of 0.1, 0.5, 1.0, 2.0, 3.0 and 4.0 g was added in each flask, covered with aluminum foil and was shaken at 180 rpm by using the contact time from 3.3.4.3. Each experiment was duplicated and the blank solution used as control. The solution was immediately filtered through filter paper. The filtrate was determined for the concentration of arsenic by ICP-AES.

3.3.5   The investigation of   the effects of competing ions on the efficiency of diatomite adsorbent in removal   As (III) and As (V) in As - spiked water

3.3.5.1 The effect of each anion on As (III) and As (V) removal

The As(III) and As(V) solution with the optimum concentration in 3.3.4.1.were prepared in 50 ml of each volumetric flask and pipette 0, 0.5, 5, 25 and 50 ml of 1000 mg/l anion standard solution ; Cl^- , NO_3^- , PO_4^{3-} and CO_3^{2-} to each volumetric flask and diluted with deionized water .A 50 ml of each was taken into 125 ml Erlenmeyer flask and   adjusted pH to the optimum pH in 3.3.4.2 by using 1 N hydrochloric acid or 1 N sodium hydroxide. The optimum weight in 3.3.4.4 of diatomite adsorbent from 3.3.3 was added in each flask, covered with aluminum foil and was shaken at 180 rpm by using the optimum contact time from 3.3.4.3. Each experiment was duplicated and the blank solution used as control. The solution was immediately filtered through filter paper. The filtrate was determined for the concentration of arsenic by ICP-AES.

3.3.5.2 The effect of mix anions on As (III) and As (V) removal

The As (III) and As (V) solution with the optimum concentration in 3.3.4.1.were prepared in 50 ml of each volumetric flask and pipette mix anions of 1000 mg/l anion standard solution; Cl^- , NO_3^- , PO_4^{3-} and CO_3^{2-} to each volumetric flask and diluted with deionized water .A 50 ml of each was taken into 125 ml Erlenmeyer flask and   adjusted pH to the optimum pH in 3.3.4.2 by using 1 N hydrochloric acid or 1 N sodium hydroxide. The optimum weight in 3.3.4.4 of diatomite adsorbent from 3.3.3 was added in each flask, covered with aluminum foil and was shaken at 180 rpm by using the optimum contact time from 3.3.4.3. Each experiment was duplicated and the blank solution used as control. The solution was immediately filtered through filter paper.   The filtrate was determined for the concentration of arsenic by ICP-AES.

3.3.6 The investigation of the efficiency of calcined diatomite in removal arsenic in arsenic contaminated surface water

Before the arsenic contaminated surface water was used. It was determined for pH, suspended solids (AWWA,1998) and concentration of total arsenic. The determination of the arsenic contaminated surface water arsenic concentration of followed standard practices for sample digestion using closed vessel microwave heating technique for determination of total metal in water (ASTM D 4309-02) the details described in appendix A.

50 ml of arsenic contaminated surface water was adjusted pH to the optimum pH in 3.3.4.2 by using 1 N sodium hydroxide. Diatomite at various weights of 0.1, 0.5, 1.0, 2.0 and 3.0 g was added in each flask, covered with aluminum foil and was shaken at 180 rpm by using the contact time from 3.3.4.3. Each experiment was duplicated and the blank solution used as a control sample. The solution was immediately filtered through filter paper. The filtrate was determined for the concentration of arsenic by ICP-AES.

The achievement of optimizing the arsenic removal condition by optimum diatomite. The comparison between the adsorption capacity of optimum diatomite in and As - spiked water and arsenic contaminated surface water was studied.

3.4 Calculation

A batch test was conducted to investigate arsenic adsorption at different concentration, pH, contact time and weight of adsorbent. The diatomite adsorbents were treated with As (III) and As (V). The filtrates were analyzed using inductively coupled plasma atomic emission spectrometry (ICP – AES) for arsenic concentration. The concentration of adsorbed As (III) or As (V) was the difference value between the initial As (III) or As (V) concentration and the total equilibrium As (III) or As (V)

concentration after adsorption. As (III) and As (V) adsorption in solution before and after experiment with calcined diatomite is calculated from:

$$\% \text{ Removal} = \left| \frac{C_i - C_f}{C_i} \right| \times 100 \tag{3.1}$$

$$\text{Adsorption capacity of adsorbent (q)} = \frac{V \times (C_i - C_f)}{W} \tag{3.2}$$

Where q is the adsorption capacity of adsorbent

   C_i is the initial As (III) and As (V) concentration (mg/l)

   C_f is the equilibrium (final) As (III) and As (V) concentration (mg / l) in the filtrate

   V   is the volume of the solution (l)

   W is the dry weight of the adsorbent (g)

CHAPTER IV

RESULTS AND DISSCUSSION

The experimental results were shown and discussed in this chapter. This chapter was divided into five sections; the first section the characteristic of the diatomite was described. The diatomite was calcined in vary condition to obtain the good yield of As (III), As (V) removal and illustrated in the second section. The third section showed the physical and chemical properties of the calcined diatomite adsorbents, the optimum conditions and the adsorption isotherm of As (III) and As (V) from arsenic- spiked water. The effects of competing anions on the efficiency of diatomite adsorbent for As (III) and As (V) removal were discovered in the fourth section. The last section was the efficiency of calcined diatomite adsorbent for As removal at optimum condition using arsenic contaminated surface water from Ron Pibun Nakorn Si Tammarat province.

4.1 The characteristic of the diatomite

Diatomite from the Mae Tha deposit Lampang province was used as adsorbent for this study. The colour of diatomite was yellowish – brown and looked like fine powdered as shown in Figure 4.1.The study of diatomite structure by using the scanning electron microscope and its microphotograph was shown in Figure 4.2. It was found that the structure of diatom had a single cylindrical with capillaries of different sizes which was benefit for the adsorbate to penetrate into the pores or outside surface of diatomite. (Borvornwattananont, 1984). The result from surface analyzer showed the specific surface area of diatomite was 65.73 m^2/g.

Figure 4.1 Lampang Diatomite
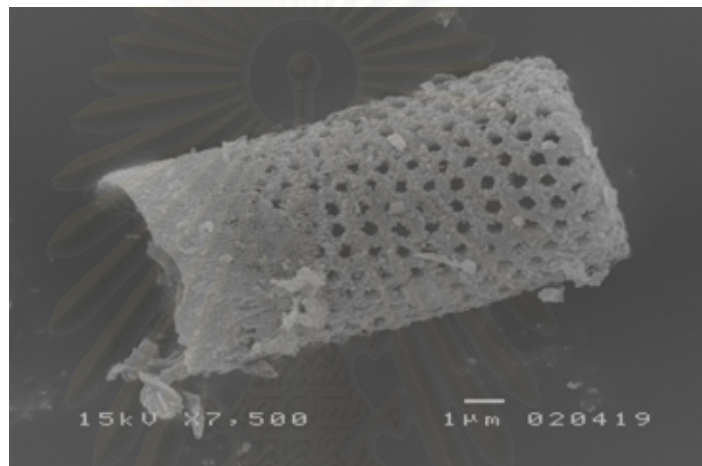
Figure 4.2 The structure of Lampang Diatomite

The chemical analysis of Lampang Diatomite by using X-Ray Fluorescence (XRF) was shown in Table 4.1. It was found that the content of SiO_2 was 79.61 % which indicated a high content of hydro silinol functional group (Si-OH) at the surface of diatomite. This caused the adsorption of diatomite with polar molecules. Considering the presence of cations such as Al, Fe, K, Mg, Ti, Na and Ca, in particular Al and Fe should have an adsorptive property on the surface of diatomite (Borvornwattananont, 1984).

Table 4.1 The chemical composition of diatomite

Compound	Conc. (%)	Compound	Conc. (%)
SiO_2	79.61	MgO	0.69
Al_2O_3	11.86	TiO_2	0.42
Fe_2O_3	3.83	Na_2O	1.03
K_2O	2.17	CaO	0.11

4.2 The effect of temperature and time on diatomite

The experiment as in chapter 3 (3.3.1.5) was designed to study the effect of temperature and time on diatomite. This study was performed at different conditions. The temperatures were varied from 200 $^{\circ}$C to 800 $^{\circ}$C and times were varied from 2 to 8 hours. Then each calcined diatomite was use for As removal. A 0.5 g of calcined diatomite was added into As – spiked water (at the concentration of 10 mgAs/l) at pH 7. For this reason, at pH 7 was represented the pH of neutral pH. The solution was shaken for 2 hrs (ASTM: D 3860 – 89a). The solution was filtered and the filtrate was determined for the concentration of arsenic by ICP-AES. The results of experimental were shown in appendix C, TableC.1.

Table 4.2 showed the removal efficiency of As (III) and As (V) depending on the temperature of calcination. The highest removal efficiency of As (III) was 79.82% at 400 $^{\circ}$C. For As (V) the highest removal efficiency was 89.25% at 800 $^{\circ}$C. From statistical analysis of the temperature of calcination, it was shown that there was significant difference between treatments at 95% confident level. The results of statistical analysis were shown in appendix B, Table B.1

Table 4.2 The effect of temperature of calcined diatomite (6 hrs) on As (III) and As (V) removal (pH 7, contact time 2 hrs and adsorbent 0.5 g)

Temperature(°C)	Arsenic removal (%)	
	As (III)	As (V)
control*	70.10±1.46 [c]	56.55±0.07 [c]
200	74.67±2.17 [b]	60.56±1.64 [b]
400	79.82±1.73 [a]	58.81±2.24 [cd]
600	61.92±1.75 [d]	54.18±1.57 [d]
800	48.38±1.97 [e]	89.25±0.58 [a]

Note: The same alphabet on the top of right corner in each row meaned there was no significant difference at 95% confident level

* control meaned untreated diatomite

Table 4.3 The effect of time at 400 °C on As (III) and 800 °C on As (V) removal

Time(hrs)	Arsenic removal (%)	
	As (III) / 400 °C	As (V) / 800 °C
control*	70.10±1.46 [a]	56.55±0.07 [a]
2	79.64±1.08 [b]	88.90±1.41 [b]
4	79.13±1.10 [b]	89.40±0.28 [b]
6	82.17±0.29 [b]	90.00±0.28 [b]
8	78.35±1.45 [b]	88.70±0.42 [b]

Note: The same alphabet on the top of right corner in each row meaned there was no significant difference at 95% confident level

* control meaned untreated diatomite

The time of calcination at the optimum temperature of calcined diatomite for As (III) and As (V) removal were shown in Table 4.3. The data indicated that the removal efficiency of As (III) and As (V) was shown to be independent of time. The highest removal efficiency of As (III) of 82.17% at 400 °C was 6 hrs. For As (V) the highest removal

efficiency of 90.00% at 800°C was found to be 6 hrs. From statistical analysis, it was shown that there was no significant difference between times of calcination in all experimental tests at 95% confident level. The results of statistical analysis were shown in appendix B, Table B.2

Figure4.3a and 4.3b illustrated the As (III) and As (V) removal which used diatomite varied temperatures and times for calcination. The results indicated that the removal of As (III) and As (V) depending on the temperature of calcination, but not on the time of calcination. For As (III) removal, the removal efficiency of As (III) increased with temperature until the maximum at 400 $^{\circ}$C .The temperature higher than 400°C resulted in efficiency decreasing. The result was similar to Yang et al. (2003) who studied the removal of urokinase on China diatomite. They found that the removal of urokinase depended on temperature in the range of 400 – 1150 $^{\circ}$C and when China diatomite was roasted over 400 $^{\circ}$C the adsorptive amount of urokinase decreased with decreasing of the specific surface area of China diatomite. The similar study was also conducted by Altandogan et al. (2002) who found that the removal of As (III) depended on temperature of heat treatment in the range of 200 $^{\circ}$C to 800°C and the maximum As (III) adsorption of red mud found when heated at 400 $^{\circ}$C. The red mud heated at temperatures higher than 400 $^{\circ}$C caused decreasing in As (III) adsorption because the pores of adsorbent could probably be clogged by some melted metal oxides. As a result, the calcined diatomite at 400°C for 6 hrs was selected in the next study for removal of As (III) and the adsorbent was called CD4006.
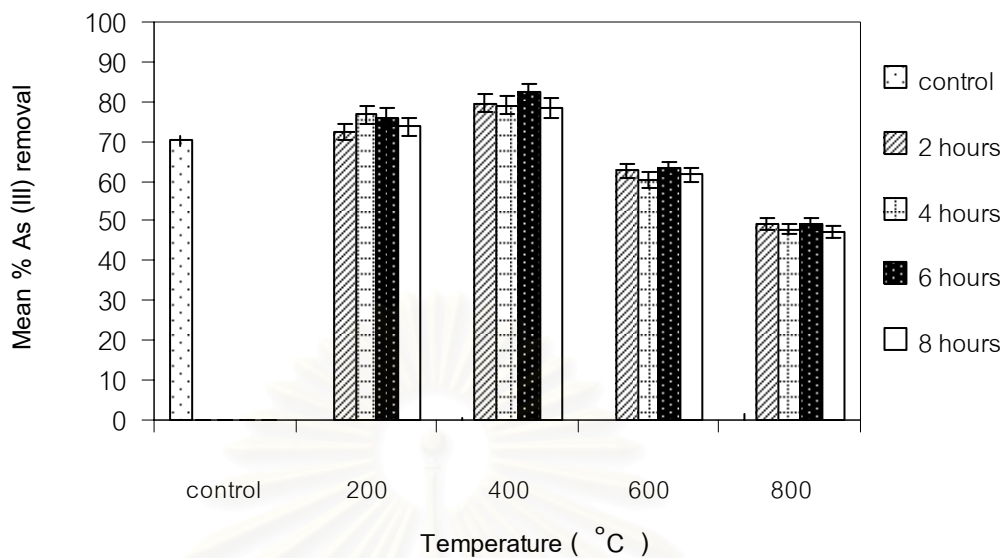
Figure 4.3a Comparison of the percentage As (III) removal at temperatures of calcination from 200°C to 800 °C and times from 2 hrs to 8 hrs (initial conc. 10 mg/l, 50 ml, pH 7, contact time 2 hrs and 0.5 g adsorbent)
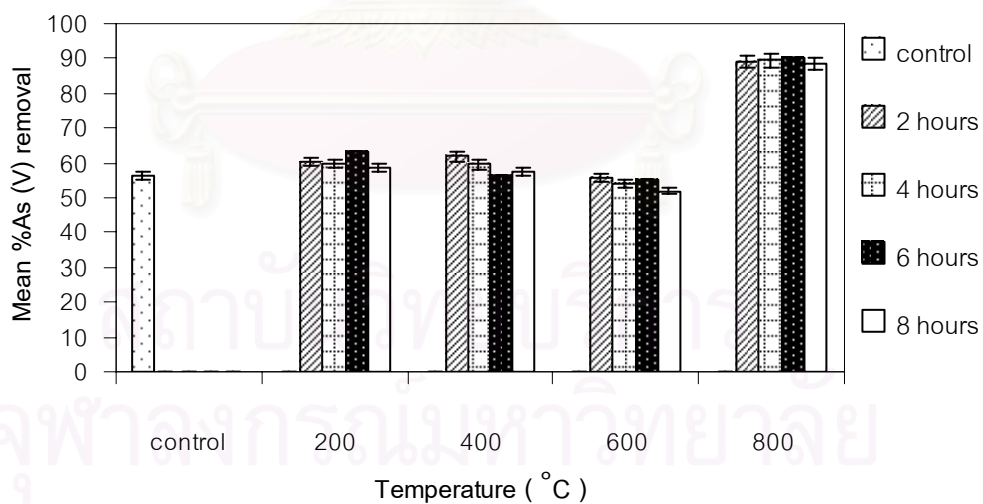
Figure 4.3b Comparison of the percentage As (V) removal at temperatures of calcination from 200°C to 800 °C and times from 2 hrs to 8 hrs (initial conc. 10 mg/l,50 ml, pH 7, contact time 2 hrs and 0.5 g adsorbent)

The removal efficiency of As (V) was more stable at 200 °C to 600°C whereas the highest mean percentage As (V) removal was 90.00% when diatomite was calcined at 800 °C as shown in Figure 4.3b. Since the outer surface area of calcined diatomite at 800 °C contained many of oxygen and small admixture of metal oxides such as aluminum oxide and iron oxides. It was possible that calcination in the present of air causing oxygen content increased. Therefore the As (V) removal efficiency by calcined diatomite at 800 °C was upon the attraction force between oxygen on the surface of calcined diatomite at 800 °C and arsenate. As a result, the calcined diatomite adsorbent at 800°C for 6 hrs was selected in the next studied for removal of As (V) and the adsorbent was called CD8006.

4.3 The physical and chemical properties of the good diatomite adsorbents

The adsorbents used in this studied were CD4006 and CD8006 as shown in Figure 4.4 and 4.5.

Lampang diatomite   CD4006

Figure 4.4 CD4006 for As (III) removal

Lampang diatomite   CD8006

Figure 4.5 CD8006 for As (V) removal

Figure 4.4 and 4.5 the diatomite before calcination was yellowish – brown powder. After calcination at 400 $^{\circ}$C it became reddish – brown powder and reddish dark brown was observed from diatomite treated at 800 $^{\circ}$C. Ullmann (2003) explained that the change in colour of calcined diatomite was the conversion of iron oxide presented as hematite (Fe_2O_3).

The results of the chemical analysis and the specific surface area of CD4006 and CD8006 were shown in Table 4.4

Table 4.4 The chemical and physical properties of CD4006 andCD8006 adsorbents

Properties	CD4006	CD8006	% CHANGE
SiO_2	76.48 %	79.04 %	+ 2.56
Al_2O_3	7.58 %	7.96 %	+0.38
Fe_2O_3	6.01%	6.26 %	+0.25
K_2O	2.89 %	3.01 %	+0.12
MgO	0.56 %	0.62 %	+0.06
TiO_2	1.28 %	1.31 %	+0.03
Na_2O	1.01 %	1.16 %	+0.15
CaO	0.61 %	0.67 %	+0.06
pH value	6	6	
Specific surface area, m^2/g	66.07	60.97	- 5.10 m^2/g

Table 4.4 showed that the content of chemical compositions of CD8006 was higher than CD4006. However, the specific surface area of CD8006 was less than

CD4006. Because the quartz (SiO_2) was transformed structure into tridymite when temperature was from 573 $^{\circ}$C to 867 $^{\circ}$C (Kongkrajan, 1996). Therefore, the surface of CD8006 was fused. In addition, the pores structures of CD8006 were covered by melted aluminum due to its melting point (660 $^{\circ}$C, Hampel, C.A., 1968).

The surface structure of CD4006 and CD8006 was analyzed by using the scanning electron microscope and their microphotographs were shown in Figure 4.6 and 4.7. Figure 4.6 illustrated that the most diatom was partially fused. It can also be seen that the surface structure of CD4006 had not changed because it was prepared at 400 $^{\circ}$C. On the other hand, at temperature of 800 $^{\circ}$C the surface structure of CD8006 was fused into lumps of cylinders and complete fusion was found.
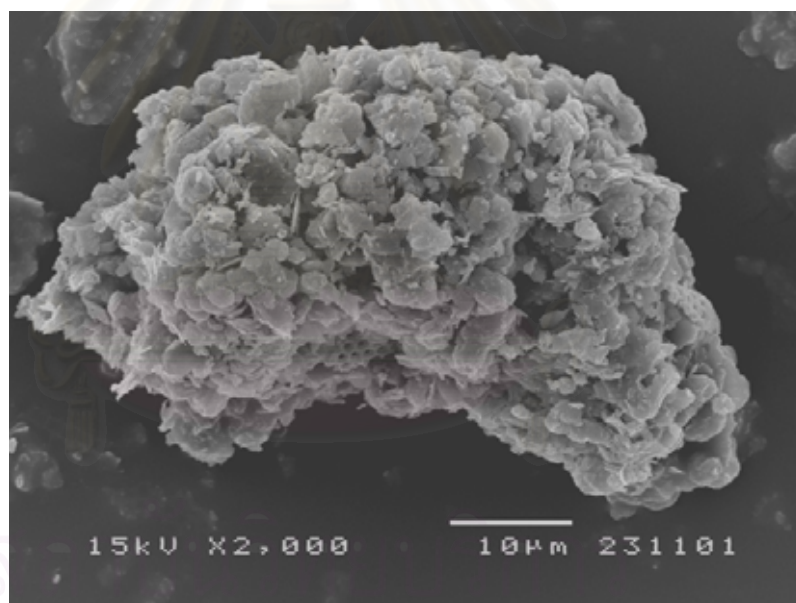
Figure 4.6 Scanning electron microscope (magnification 2000 x) of CD4006
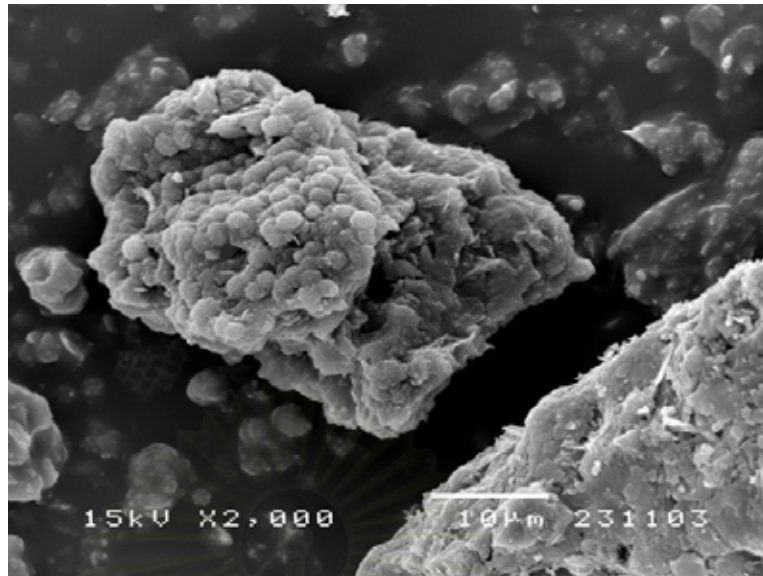
Figure 4.7 Scanning electron microscope (magnification 2000 x) of CD8006

4.4 The optimum conditions, the adsorption isotherm of As (III) and As (V) from As - spiked water and the effects of competing anions on the efficiency of diatomite for As (III) and As (V) removal

    4.4.1 The optimum condition of As (III) and As (V) removal in arsenic- spiked water using CD4006 and CD8006 by varying the concentration, pH, the contact time and the amount of diatomite

        4.4.1.1 The efficiency of diatomite CD4006 and CD8006 on As (III) and As (V) removal by varying concentration

        The efficiency of diatomite CD4006 and CD8006 on As (III) and As (V) removal was studied. The concentrations of As - spiked water in this studied were varied from 0.5 – 10 mg/L at pH 7 and the contact time was 2 hrs. The adsorbent used was 0.5 g. The results of experimental were shown in appendix C, TableC.2

The results from this studied were shown in Table 4.5 and Figure 4.8. It was found that CD4006 andCD8006 adsorbents could adsorb As (III) and As (V) in the range of 0.5 - 10 mg/L. The percentage removal of As (III) was 79.0% - 84.4% at the concentration of 0.5, 1, 2, 5 and 10 mg/L. The maximum percentage removal of As (III) was 84.45%. The percentage removal of As (V) was 86.0% - 90.0% and the maximum percentage removal of As (V) was 90.05%. From statistical analysis, it was shown that there was no significant difference between treatments at 95% confident level. The results of statistical analysis were shown in appendix B, Table B.3

It was found that the percentage removal of As (III) and As (V) increased with increasing concentration (figure 4.8). These results similar to Lenoble et al. (2002) who studied As (III) and As (V) removal by goethite he found that As (III) and As (V) removal increased as the concentration of As increased from 0 to 30 mg/L.Boontae (2003) studied As (V) removal by calcined diatomite at 800 $^{\circ}$C for 8 hrs she found that the optimum concentration of arsenic was 30 mg/L. In addition, As (V) was effectively removed by CD8006 more than As (III) removed by CD4006 due to the different adsorption mechanism.

Table 4.5 The efficiency of diatomite CD4006 and CD8006 on As (III) and As (V) removal by varying the concentration (pH 7, contact time 2 hrs and adsorbent 0.5 g)

Concentration(mg/L)	Arsenic removal (%)	
	CD4006:As (III)	CD8006:As (V)
0.5	79.00±4.24 [a]	86.00±2.83 [a]
1	81.00±1.41 [a]	86.50±2.12 [a]
2	82.00±1.41 [a]	88.75±0.35 [a]
5	83.80±0.57 [a]	89.90±0.42 [a]
10	84.45±0.07 [a]	90.05±0.07 [a]

Note: The same alphabet on the top of right corner in each row meaned there was no significant difference at 95% confident level of each concentration
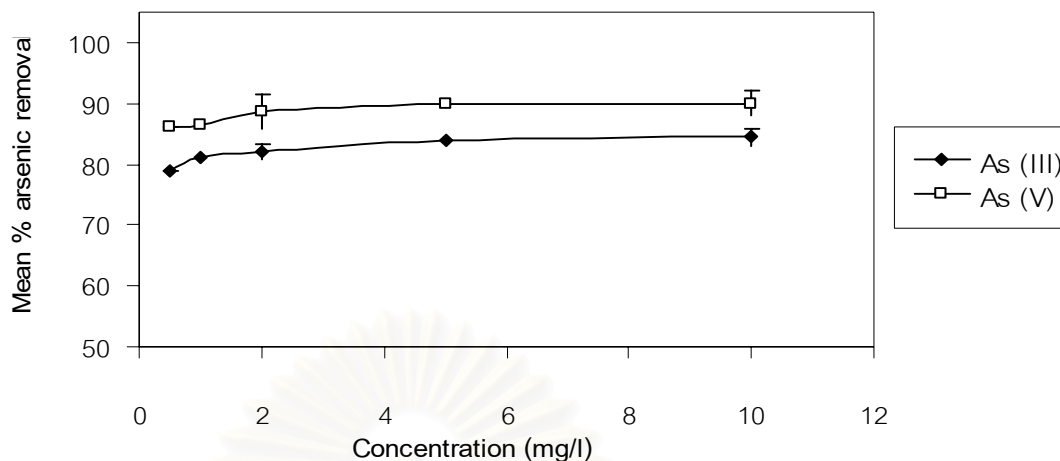
Figure 4.8 Comparison of percentage removal of As (III) and As (V) at difference concentration

From this studied it should be noted that the As (III) and As (V) removal efficiency were not depended on concentration. The maximum percentage removal of As (III) and As (V) were 84.45% and 90.05 % respectively. Therefore the optimum concentration of 10mg/L was chosen for the following experiments.

4.4.1.2 The efficiency of diatomite CD4006 and CD8006 on As (III) and As (V) removal by varying pH

The effect of pH on As (III) and As (V) removal was studied at the optimum concentration 10 mg/L from 4.4.1.1. The pH value in this studied were varied from 4 to 9. The 2 hrs contact time and 0.5 g of adsorbent was used. The results of experimental were shown in appendix C, TableC.3. The results from this studied were shown in Table 4.6 and Figure 4.9. It was found that CD4006 andCD8006 adsorbents could adsorb As (III) and As (V) in the range of pH 4, 5, 6, 7, 8 and 9.

Table 4.6 The efficiency of diatomite CD4006 and CD8006 on As (III) and As (V) removal by varying pH (Concentration of As (III) and As (V) 10 mg/L, contact time 2 hrs and adsorbent 0.5 g)

pH (Before)	pH (After)		Arsenic removal (%)	
	As (III)	As (V)	As (III)	As (V)
4	4.87	4.90	84.73$\pm$0.14 [a]	89.70$\pm$0.42 [ab]
5	5.08	4.97	85.14$\pm$0.14 [a]	90.00$\pm$0.28 [a]
6	5.20	5.13	83.25$\pm$0.36 [b]	89.65$\pm$0.07 [ab]
7	5.24	5.30	83.20$\pm$0.29 [b]	89.65$\pm$0.07 [ab]
8	5.28	5.44	83.09$\pm$0.29 [b]	89.45$\pm$0.07 [ab]
9	5.46	5.44	81.05$\pm$0.14 [c]	89.30$\pm$0.14 [b]

Note: The same alphabet on the top of right corner in each row meaned there was no significant difference at 95% confident level of each pH

The percentage removal of As (III) was from 81.0% - 85.1% and the maximum percentage removal of As (III) was 85.14% at pH 5. The percentage removal of As (V) was from 89.3% - 90.0%. The maximum percentage removal of As (V) was 90.00% at pH 5. It was shown that there was significant difference in statistic between pH at 95% confident level for As (III) removal. However, for As (V), it was shown that there was no significant difference between pH at 95% confident level. The results of statistical analysis were shown in appendix B, Table B.4
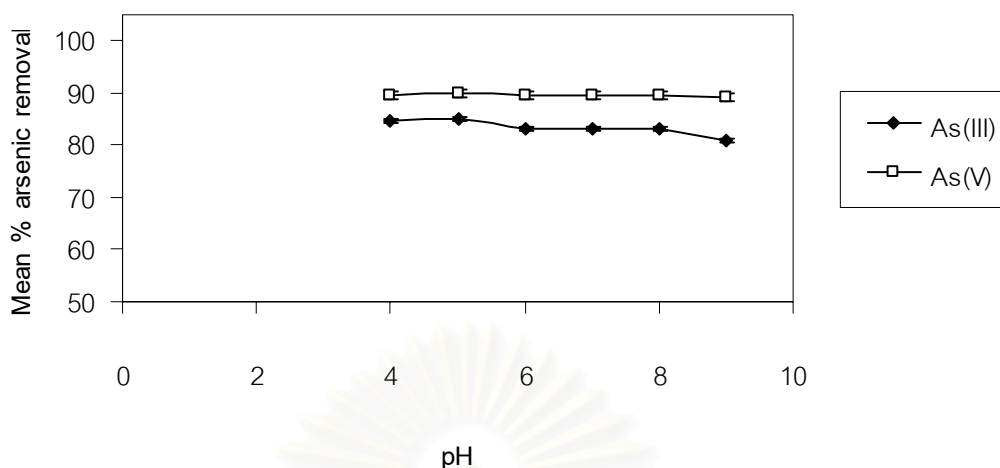
Figure 4.9 Comparison of percentage removal of As (III) and As (V) at difference pH

From Figure 4.9, it was found that the percentage removal of As (III) decreased as the pH value increased from 6 – 9. Whereas the pH did not significantly effect the removal of As (V). The optimum pH for As (III) and As (V) removal were 4 -5. As a result, it was similar to the study of Ladeira and Ciminelli (2003) who reported the arsenic removal increased with decreasing pH. They also found both As (III) and As (V) were efficiently removed by goethite in the optimum pH of 5.5.

The effect of pH on the removal of As may be explained that, the hydroxyl group on surface of diatomite became positively charged or negatively charged when pH changed as shown in equation 4.1 and 4.2

$$H^+ + SOH \rightleftharpoons SOH_2^+ \qquad (4.1)$$

$$OH^- + SOH \rightleftharpoons H^+ + SO^{-2} \qquad (4.2)$$

SOH = Surface hydroxide

The surface hydroxide gained proton at low pH thus, the charge of surface was positive (4.1). At high pH, the surface hydroxide lost proton, the surface became negatively charged. When the concentration of SOH_2^+ site equaled to the concentration of SO^{-2} site, the average surface charge was neutral at the zero point of charge (ZPC). Ghoti, et al. (2003) found that zero point charge of diatomite occurred at

pH 5.8. Below this pH, diatomite had a net positive charge resulting in a preference for adsorption of anions.

For As (III) removal, there were 2 equations to explain the dissociation of As (III) in aqueous solution as following:

$$H_3AsO_3 + H_2O \rightleftharpoons H_2AsO_3^- + H_3O^+ : pKa_1 = 9.20 \qquad (4.3)$$

$$H_2AsO_3^- + H_2O \rightleftharpoons HAsO_3^{2-} + H_3O^+ : pKa_2 = 12.13 \qquad (4.4)$$
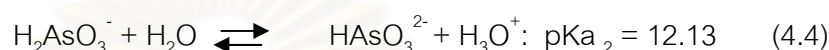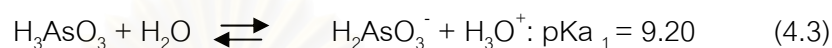
The adsorption of As (III) by CD4006 occurred on the surface of CD4006 which the mechanism of adsorption was represented by equations (Xiaoguan M.et al, 2000):

$$SOH + H_3AsO_3 \rightleftharpoons SHAsO_3 + H_2O \qquad (4.5)$$

$$SOH + H_3AsO_3 \rightleftharpoons SHAsO_3^- + H_2O + H^+ \qquad (4.6)$$
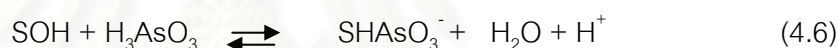
From the equation 4.6, it was indicated that As (III) can be adsorbed in the wide pH range because As (III) was uncharged in form H_3AsO_3 at pH 2 – 10 (Lenoble et.al, 2002). The efficiency of As (III) removal was depending on the attraction force on the surface of adsorbent. According to the results of Lenoble et.al (2002) who reported that the optimum pH for As (III) by pillared clays was obtained at 4< pH< 9. For pH value above 10, the pillared clays were damaged and decreased in adsorption. Singh and Pant (2003) determined the optimum pH for adsorption of As (III) on activated alumina. The results indicated that the maximum adsorption (94.4%) was achieved in the pH range of 6.0 – 8.0 for initial As (III) concentration of 0.5 mg/L. Benjamin et al. (1998) also reported that sorption of As (III) by pillared clays was dependence on pH.

Regarding As (V) removal, there were 3 equations to explain the dissociation of As (V) in aqueous solution as following:

$$H_3AsO_4 + H_2O \rightleftharpoons H_2AsO_4^- + H_3O^+ : pKa_1 = 2.20 \qquad (4.8)$$

$$H_2AsO_4^- + H_2O \rightleftharpoons HAsO_4^{2-} + H_3O^- : pKa_2 = 6.97 \qquad (4.9)$$

$$HAsO_4^{2-} + H_2O \rightleftharpoons AsO_4^{3-} + H_3O^+: \quad pKa_3 = 11.53 \qquad (4.10)$$
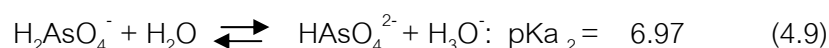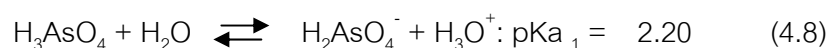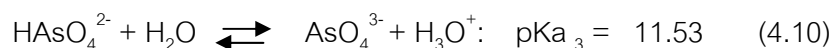
From the results could be explained that the adsorption occurred at the surface sites of adsorbent (CD8006). The mechanisms for the uptake of As (V) on to oxides surface were shown as following (Meng et al., 2003):

$$SOH + H_3AsO_4 \rightleftharpoons SH_2AsO_4 + H_2O \qquad (4.11)$$

$$SOH + H_3AsO_4 \rightleftharpoons SHAsO_4^- + H_2O + H^+ \qquad (4.12)$$

$$SOH + H_3AsO_4 \rightleftharpoons SAsO_4^{2-} + H_2O + 2H^+ \qquad (4.13)$$
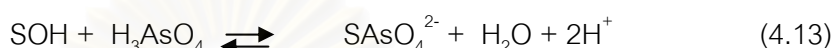
In adsorption process, the metal oxides on the surface of CD8006 especially iron oxide which had a positive surface charge and preferentially adsorbed As(V).

Zhange et al. (2003) who studied the effect of equilibrium pH on As (V) removal by iron based cerium ions adsorbent. They found that the efficiency of adsorption increased at the pH decreased. The optimum pH for As (V) removal by natural iron ores was between 4.5 to 6.5. Lenoble et al. (2002) who also reported that the As (III) and As (V) removal at pH 3 to 11. Results indicated increasing pH from 3 to 11 had almost no effect on sorption of As (III) and As (V) on goethite.

In addition, ferric arsenate was stability and insoluble in water. Vircikova et al. (1995) who studied the solubility of ferric arsenate precipitates at a pH of 2 to 10. They found that at temperature of 23 $^{\circ}$C a minimum (less than 1 mg/L) ferric arsenate solubility at pH 3 to 8 and the solubility of ferric arsenate increased in the strongly acid or alkaline conditions. Krause and Ettel (1989) studied the solubility and stability of ferric arsenate compounds. They found that the solubility of ferric arsenate decreased with increasing Fe/As ratios. At Fe/As ratio=8 had solubility <1 mg /L between pH 3 to 8 and The As solubility did not increase during aging over a 2–3.7 years period. Therefore, arsenic compound in form Fe-As was stable in the natural pH. It should be noted that the sediment of Fe-As could be treated with sanitary landfill due to it was little leached into environment. The results of comparison of As (III) removal by CD4006 adsorbent and As (V) removal by CD8006 adsorbent were almost a constant value in a pH

between 4 and 9 and the percentage As (V) removal were effectively removed more than As (III) CD4006 because the mechanisms of adsorption were difference.

From this study the 80 % of As (III) and As (V) removal efficiency can be removed and were depended on pH. Therefore the optimum pH 5 was chosen for the following experiments.

4.4.1.3 The efficiency of diatomite CD4006 and CD8006 on As (III) and As (V) removal by varying contact time

The effect of contact time on As (III) and As (V) removal was studied at the optimum concentration 10 mg/L from 4.4.1.1. The optimum pH in this studied was 5.

The contact time was varied from 30 min to 420 min and 0.5 g of adsorbent was used. The results of experimental were shown in appendix C, TableC.4.

The results from this studied were shown in Table 4.7 and Figure 4.10. It was found that CD4006 andCD8006 adsorbents could adsorb As (III) and As (V) at the contact time from 30 min to 420 min. The percentage removal of As (III) were from 84.5% - 86.6% and the maximum percentage removal of As (III) was 86.78% at contact time 300 min. For As (V), the percentage removals of As (V) were from 89.9% -91.3 % and the maximum percentage removal of As (V) was 91.30% at contact time 300 min. It was shown that there was significant difference in statistic between contact times at 95% confident level. The results of statistical analysis were shown in appendix B, Table B.5

Table 4.7 The efficiency of diatomite CD4006 and CD8006 on As (III) and As (V) removal by varying contact time (Concentration of As (III) and As (V) 10 mg/L, pH 5 and 0.5 g adsorbent)

Contact time(min)	Arsenic removal (%)	
	As (III)	As (V)
30	84.53±0.14 [a]	89.95±0.07 [a]
60	84.94±0.14 [a]	90.20±0.00 [ab]
90	85.14±0.14 [b]	90.50±0.14 [ab]
120	85.04±0.29 [a]	90.50±0.14 [ab]
150	85.96±0.14 [b]	90.40±0.00 [ab]
180	86.17±0.14 [b]	90.60±0.28 [ab]
240	86.37±0.14 [b]	91.20±0.28 [ab]
300	86.58±0.14 [b]	91.30±0.14 [b]
360	86.58±0.14 [b]	91.20±0.28 [b]
420	86.58±0.14 [b]	91.10±0.42 [b]

Note: The same alphabet on the top of right corner in each row meaned there was no significant difference at 95% confident level of each contact time

It was found that the percentage removal of As (III) and As (V) slightly increased with contact time from 30min to 240 min (figure 4.10). The optimum contact time for removal As (III) and As (V) in this study were selected at 300 min. A similar result was described by Lenoble et al. (2002) who studied As (III) and As (V) removal by goethite he found that after 4 hrs the adsorption of As (III) and As (V) on goethite was stable. In addition, this optimum time of 300 min was in agreement with Altandogan et al. (2000) who studied the effect of contact time on adsorption at optimum pH for As (III) and As (V) removal on red mud. He observed that the removal of As (III) and As (V) increased with time (from 30 to 270 min) and was constant in 45 and 90 min, respectively.
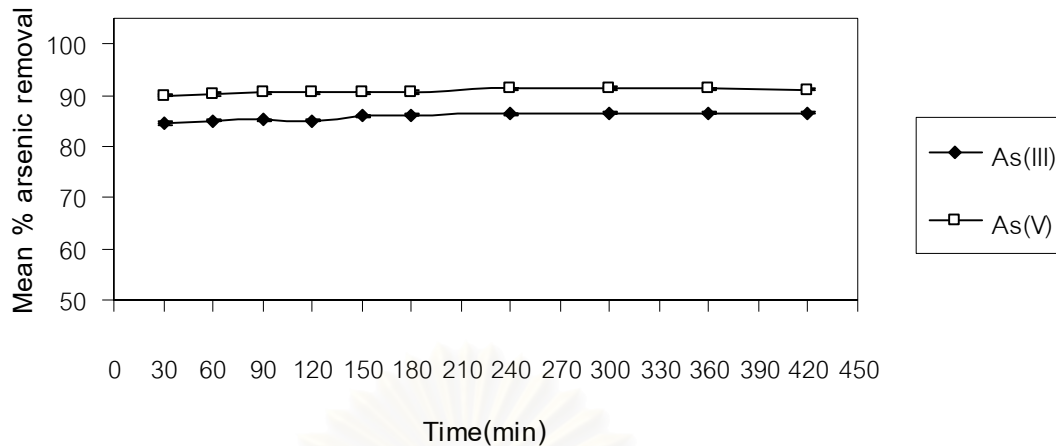
Figure 4.10 Comparison of percentage removal of As (III) and As (V) at difference contact time

From this studied it should be noted that the As (III) and As (V) removal efficiency depended on the contact time. Therefore, an optimum time of 300 min was chosen for the following experiments.

4.4.1.4 The efficiency of diatomite CD4006 and CD8006 on As (III) and As (V) removal by varying amount of adsorbent

The effect of the amount of adsorbent on As (III) and As (V) removal was studied at the optimum concentration 10 mg/L from 4.4.1.1. The optimum pH 5 from 4.4.4.2, the contact time 300 min from 4.4.4.3.In this studied the amount of adsorbent were varied from 0.1 g to 4.0 g. The results of experimental were shown in appendix C, TableC.5.

The results from this studied were shown in Table 4.8 and Figure 4.1. It was found that CD4006 andCD8006 adsorbents could adsorb 0.5 mg of As (III) and As (V) using the amount of adsorbent varied from 0.1 g to 4.0 g. The percentage removal of As(III) were from 69.3% - 99.5% and the maximum percentage removal of As(III) was 99.49% by using CD4006 adsorbent 4 g . For As (V), the percentage removal of As (V) were from 70.3% - 99.6% and the maximum percentage removal of As (V) was 99.60% by using CD8006 adsorbent 4 g. It was shown that there was significant difference in

statistic between the amounts of adsorbent at 95% confident level. However at the amount of adsorbent of 3 – 4 g had no significant difference at 95 % confident level. The results of statistical analysis were shown in appendix B, Table B.6

Table 4.8 The efficiency of diatomite CD4006 and CD8006 on As (III) and As (V) removal by varying amount of adsorbent (Concentration of As (III) and As (V) 10 mg/L, pH 5, contact time 300 min)

Amount of adsorbent (g)	Arsenic removal (%)	
	As (III)	As (V)
0.10	69.26 ± 0.29 [a]	70.30 ± 0.14 [a]
0.50	86.37 ± 0.14 [b]	91.80 ± 0.14 [b]
1.00	93.44 ± 0.29 [c]	95.10 ± 0.14 [c]
2.00	96.62 ± 0.14 [d]	98.10 ± 0.14 [d]
3.00	98.72 ± 0.22 [e]	99.05 ± 0.07 [e]
4.00	99.49 ± 0.00 [e]	99.60 ± 0.14 [e]

Note: The same alphabet on the top of right corner in each row meaned there was no significant difference at 95% confident level of each amount of adsorbent
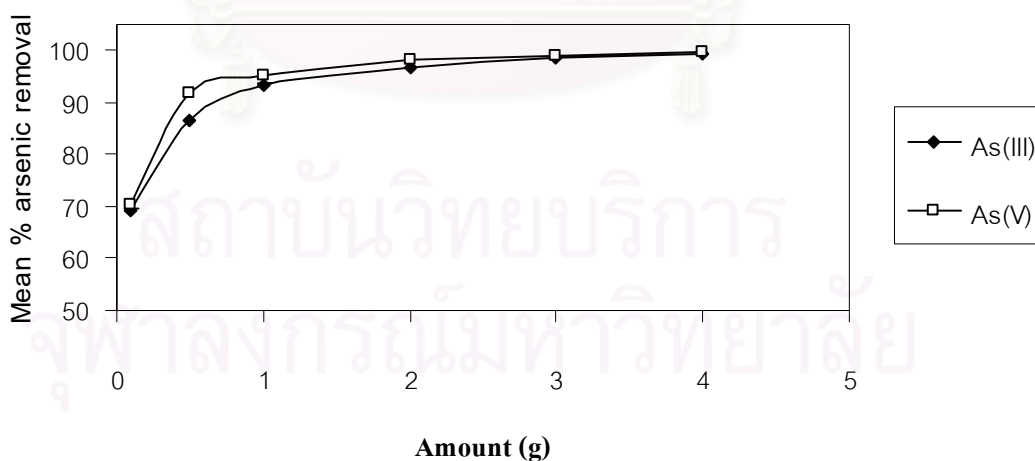
Figure 4.11 Comparison of percentage removal of As (III) and As (V) at difference amount of adsorbent

From Figure 4.11, it was found that the percentage removal of As (III) and As (V) increased with the amount of adsorbent. The percentage removal was from 69% to 86.1%for As (III) and from 70 – 92% for As (V) when the amount of CD4006 and CD8006 were changed from 0.5 g to 1 g after that they were slightly increased with the amount of adsorbent of 3.0 g.Therefore, the optimum amount of adsorbent for removal As (III) and As (V) were 3.0 g. A similar result was described by Singh et al. (2003) who studied the adsorption capacity of activated alumina for adsorption of As (III) by varying the amount of adsorbents from 0 to 1 g. He found that adsorption increased with the adsorption was 93 % As (V) removal when 13g/L of activated alumina was used.

The result from this studied should be noted that the As (III) and As (V) removal efficiency were depended on the amount of adsorbent. Therefore the amount of adsorbent 3.0 grams was chosen for the following experiments.

4.4.2 The adsorption isotherm of As (III) and As (V) from As - spiked water

The adsorption isotherm was carried out to determine the maximum capacity of As (III) and As (V) adsorbed over CD4006 and CD8006 adsorbent. The isotherm experiment was conducted at optimum conditions as follow :concentration of As(III) and (V) of 10 mg/L (separately), pH 5, contact time 300 min and 0.5g to 4 g of CD4006 and CD8006 adsorbent for As(III) and As(V) adsorption . The results of experimental were shown in appendix C, TableC.11 and C.12.

The distribution of As (III) and As (V) between the liquid phase and the solid adsorbent phase were measured for the adsorption process and can be expressed by isotherm models. There were two models using in this experiment: Freundlich and Langmuir isotherms. The equilibrium data were fitted to Freundlich and Langmuir equation in the linear form. Freundlich equation was as follows:

$$\text{Log } [x/m] = \log (K) + [1/n] \log (Ce) \tag{4.14}$$

Where x is the amount of solute adsorbed (mg), m the mass of adsorbent used (g), Ce the equilibrium solute concentration in solution (mg/L), and K and n the constants representing the adsorption capacity (mg/g) and intensity of the adsorbent, respectively. The values of K and n were obtained from the slope and intercept of the plot between log (x/m) and log Ce and were shown in Table 4.9.

Langmuir equation was applied to quantify adsorption capacity and was given as follows:

$$(1/q) = (1/bqmCe) + (1/qm) \qquad\qquad (4.15)$$

Where Ce and q were equilibrium solute concentration (mg/l) and equilibrium adsorption capacity, respectively (mg/g), qm and b the Langmuir constants representing adsorption capacity (mg/g) and energy of adsorption (L/mg), respectively. The value of qm and b were calculated from the slope and intercept of the linear plot of (1/qe) versus (1/Ce) and were reported in Table 4.10.

The Fruendlich and Langmuir isotherm were plotted for adsorption of As (III) on CD4006 adsorbent and As (V) on Cd8006 adsorbent as shown in Figure 4.12 to 4.15, respectively. Based on the values of correlation coefficients (r^2), it should be noted that the r^2 value was relate to the nature of isotherm type; unfavorable ($r^2 > 1$), linear ($r^2 = 1$), favorable ($0 < r^2 < 1$) or irreversible ($r^2 = 0$) (Khraisheh, Yahya and Wendy, 2003)
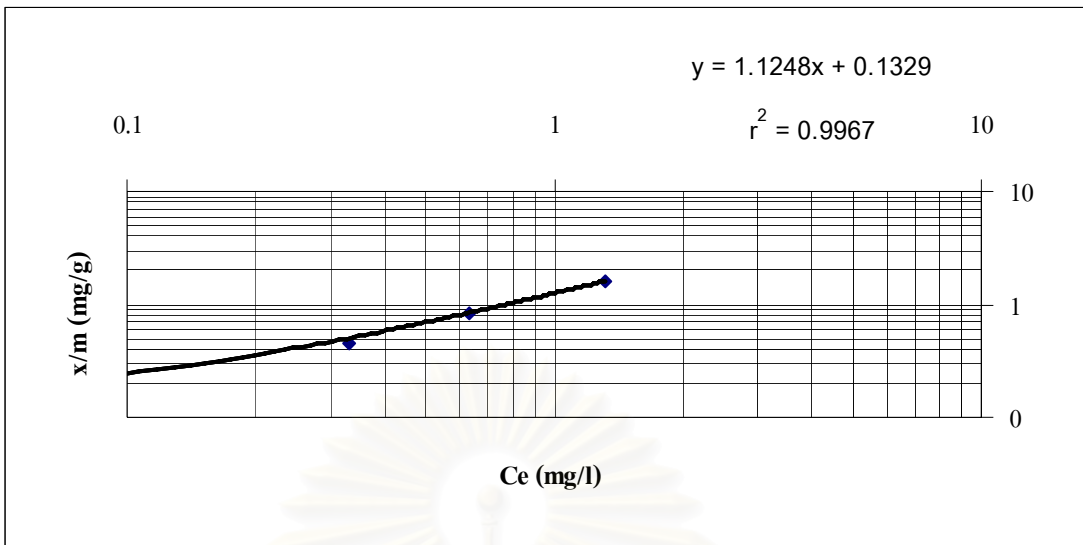
Figure 4.12 The Fruendlich Isotherm of As (III) removal using CD4006 adsorbent
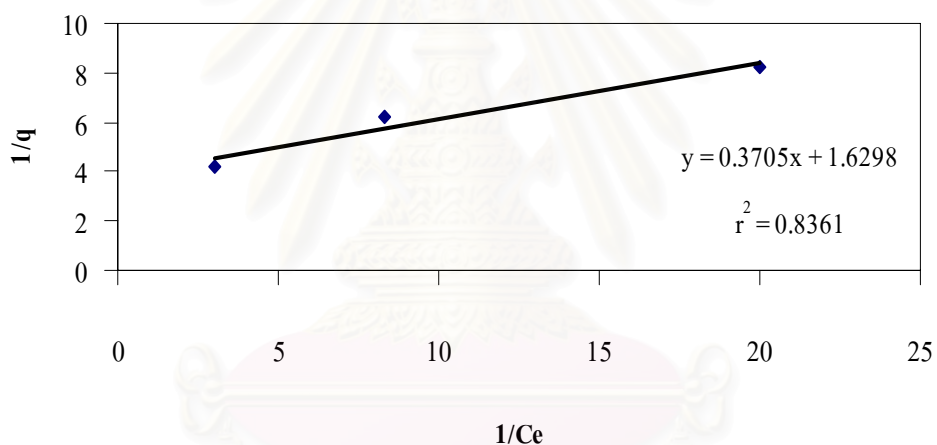
Figure 4.13 The Langmuir Isotherm of As (III) removal using CD4006 adsorbent

From Figure 4.12 and 4.13, in comparison of two adsorption model for As (III) adsorption it was found that the r^2 of Fruendlich isotherm was higher than Langmuir isotherm as shown in Table 4.9.Regarding As (V) adsorption as shown in Figure 4.14 and 4.15, the result of As (III) adsorption was similar to As (V) adsorption. It was found that the r^2 of Fruendlich isotherm was higher than Langmuir isotherm (Table 4.9).
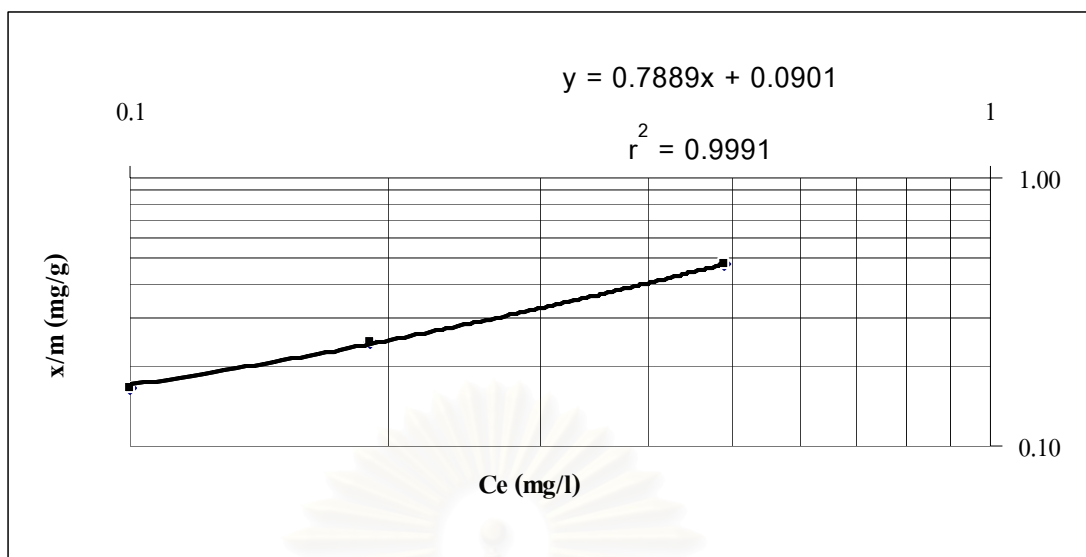
y = 0.7889x + 0.0901

r^2 = 0.9991

Figure 4.14 The Fruendlich Isotherm of As (V) removal using CD8006 adsorbent

y = 0.3886x + 1.1352

r^2 = 0.9142
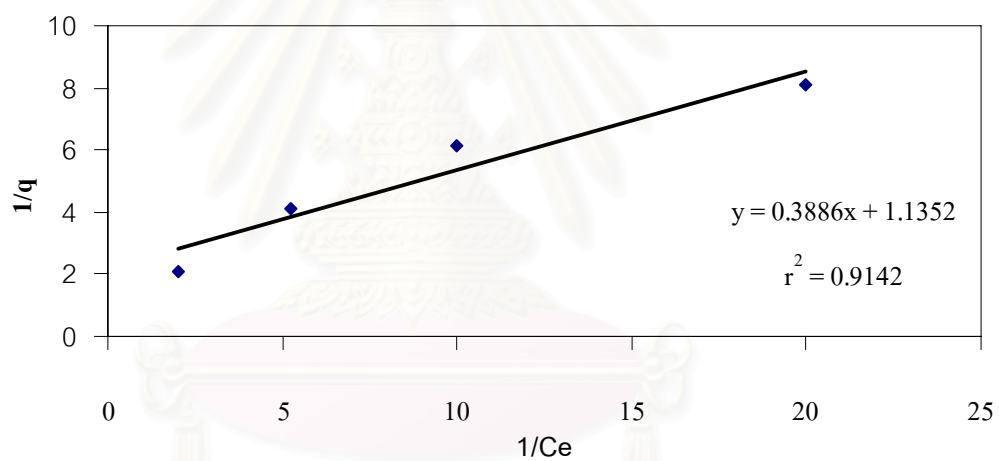
Figure 4.15 The Langmuir Isotherm of As (V) removal using CD8006 adsorbent

Table 4.9 The r^2 of Fruendlich and Langmuir Isotherms for As (III) and As (V) removal

Isotherm	r^2 of isotherm	
	As(III)	As(V)
Fruendlich	0.9967	0.9991
Langmuir	0.8361	0.9142

The linear equations in Figure 4.12 and 4.14 were used to determine the Fruendlich isotherm constants such as K and 1/n which these constants can be determined the maximum adsorption capacity (q_{max}) from Fruendlich isotherm equation. The Fruendlich isotherm constants and adsorption capacity were shown in Table 4.10.

The value of K and 1/n representing the adsorption ability and intensity of the adsorbent were shown in Table 4.10. The adsorption capacity of As (III) by CD4006 adsorbent and As (V) by CD8006 adsorbent were 1.77 mg/g and 0.55 mg/g. The calculation examples for determined the q_{max} based on the Freundlich equation were shown in appendix C.

Table 4.10 The Freundlich isotherm constants and the adsorption capacity of As (III) andAs (V) (Concentration 10 mg/L, 50ml, pH 5 and contact time 300 min)

Species	Adsorbent	Freundlich constants		r^2	Adsorption capacity : q_{max} (mg/g)
		K	1/n		
As(III)	CD4006	1.1248	0.1329	0.9967	1.77
As(V)	CD8006	0.7889	0.0901	0.9991	0.55

As a result, the adsorption isotherm for As (III) and As (V) were fitted Fruendlich isotherm. It was found that As (III) and As (V) adsorbed on CD4006 and CD8006 belonged to multilayer adsorption. This result similar to Junsomboon (2001) who studied As (III) and As (V) adsorption by red clay he reported that As(III) and As(V) adsorption conformed to Fruendlich isotherm at pH 4 and detention time at 24 hour.

4.5 The effects of competing anions on the efficiency of diatomite adsorbent for As (III) and As (V) removal

4.5.1 The effects of competing anions on the efficiency of CD4006 adsorbent for As (III) removal

The effects of anions on As (III) removal were evaluated in arsenic – spike water. Phosphate, nitrate, carbonate and chloride were added separately into the solution in the range of concentration of 10 to 1000 mg/L. The optimum conditions for this studied was as follows: pH 5, contact time 300 min. and 3.0 g of CD4006 adsorbent. The results of experimental were shown in appendix C, TableC.6 – C9.

The results from this studied were shown in Table 4.11 and Figure 4.16. It was found that at the concentrations of PO_4^{3-}, NO_3^{2-}, CO_3^{2-} and Cl^- varied from 10 mg/l to 1000 mg/l, the percentage removal of As(III) were from 94.4% - 98.8%.

Table 4.11 The effect of competing anion: PO_4^{3-} , NO_3^{2-} , CO_3^{2} and Cl^- on As (III) removal

Concentration (mg/l)	As (III) removal (%)			
	PO_4^{3-}	NO_3^{2-}	CO_3^{2-}	Cl^-
0	98.77±0.14 [a]	98.77±0.14 [a]	98.77±0.14 [a]	98.77±0.14 [a]
10	96.57±0.51 [a]	97.69±0.07 [a]	97.28±0.22 [a]	97.39±0.07 [a]
100	94.98±0.00 [b]	97.64±0.14 [a]	97.34±0.00 [a]	97.28±0.07 [a]
500	94.72±0.07 [b]	97.69±0.07 [a]	97.44±0.00 [a]	97.44±0.14 [a]
1000	94.42±0.36 [b]	97.80±0.07 [a]	97.34±0.14 [a]	97.39±0.07 [a]

Note: The same alphabet on the top of right corner in each row meaned there was no significant difference at 95% confident level

From statistical analysis, it was shown those anions: nitrate, carbonate and chloride were not significant difference between treatments at 95% confident level. However, phosphate was significant difference between treatments at 95% confident level. The results of statistical analysis were shown in appendix B, Table B.7 – B.10
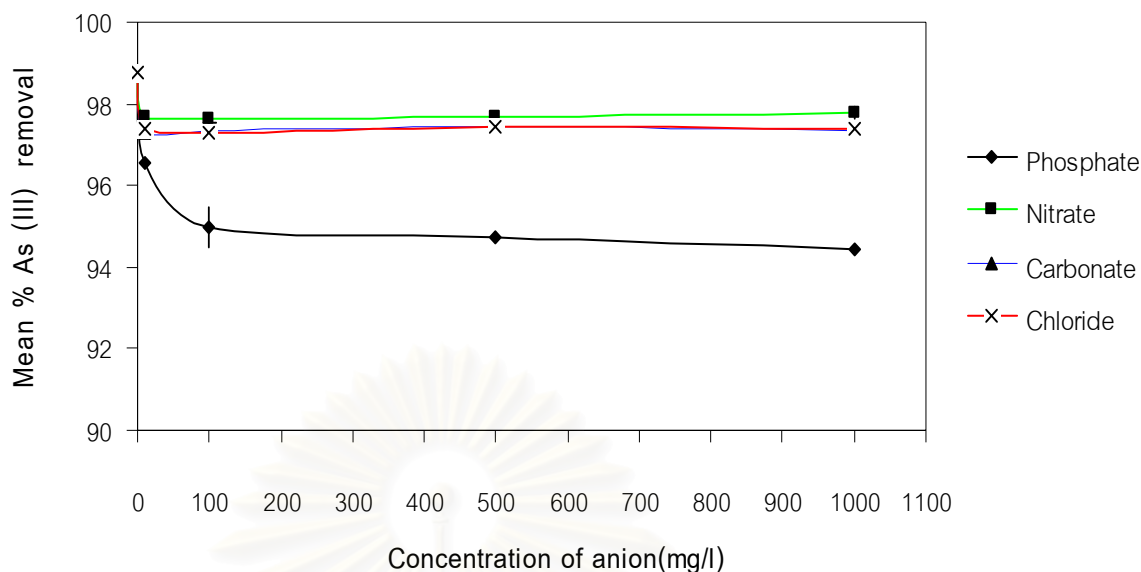
Figure 4.16 The comparison of the effect of anions on As (III) removal by CD4006 adsorbent

The comparison of the effect of each anions on As (III) removal were shown in Figure 4.16.The result showed that the addition of nitrate, carbonate and chloride were not affected the As(III) removal,   while the As(III) removal was significantly decreased by the addition of phosphate ion. Because the adsorption affinity of As (III) for CD4006 adsorbent was less than the adsorption affinity of phosphate. In addition, Meng et al. (2003) suggested that As (III) had low affinity for iron hydroxide surface sites but phosphate occupied the highly active surface sites because of its higher adsorptive affinity than As (III).Therefore; Phosphate could substantially reduce the removal of As (III). This result was related to Kofiatis et al. (2002) who studied the effects of phosphate on the removal of As(III) .Their result showed that phosphate could significantly reduced the removal of As(III) by using iron hydroxide as adsorbent..

4.5.2 The effects of competing anion on the efficiency of CD8006 adsorbent for As (V) removal

The effects of anions on As (V) removal were evaluated in arsenic – spike water. Phosphate, nitrate, carbonate and chloride were added separately into the solution in the range of concentration of 10 to 1000 mg/l. The optimum conditions for

this studied was as follows: pH 5, contact time 300 min. and 3.0 g of CD8006 adsorbent. The results of experimental were shown in appendix C, TableC.6 – C9.

Table 4.12 The effect of competing anion: PO_4^{3-}, NO_3^{2-}, CO_3^{2} and Cl^- on As (V) removal

Concentration (mg/l)	As (V) removal (%)			
	PO_4^{3-}	NO_3^{2-}	CO_3^{2}	Cl^-
0	99.05±0.07 [a]	99.05±0.07 [a]	99.05±0.07 [a]	99.05±0.07 [a]
10	98.40±0.14 [a]	98.40±0.14 [a]	98.80±0.28 [a]	99.00±0.14 [a]
100	98.20±0.14 [a]	98.30±0.00 [a]	99.05±0.07 [a]	99.00±0.14 [a]
500	98.05±0.07 [a]	98.35±0.07 [a]	98.35±0.07 [a]	98.65±0.21 [a]
1000	97.30±0.14 [b]	98.35±0.07 [a]	98.55±0.07 [a]	98.65±0.07 [a]

Note: The same alphabet on the top of right corner in each row meaned there was no significant difference at 95% confident level

The results from this studied were shown in Table 4.12 and Figure 4.17. It was found that at the concentrations of phosphate varied from 10 mg/l to 1000 mg/l, the percentage removal of As(V) were from 97.3 % - 99.05 %.

From statistical analysis, it was shown those anions: nitrate, carbonate and chloride were not significant difference between treatments at 95% confident level. However, phosphate at concentration 1000 mg/l was significant difference between treatments at 95% confident level. The results of statistical analysis were shown in appendix B, Table B.7 – B. 10.
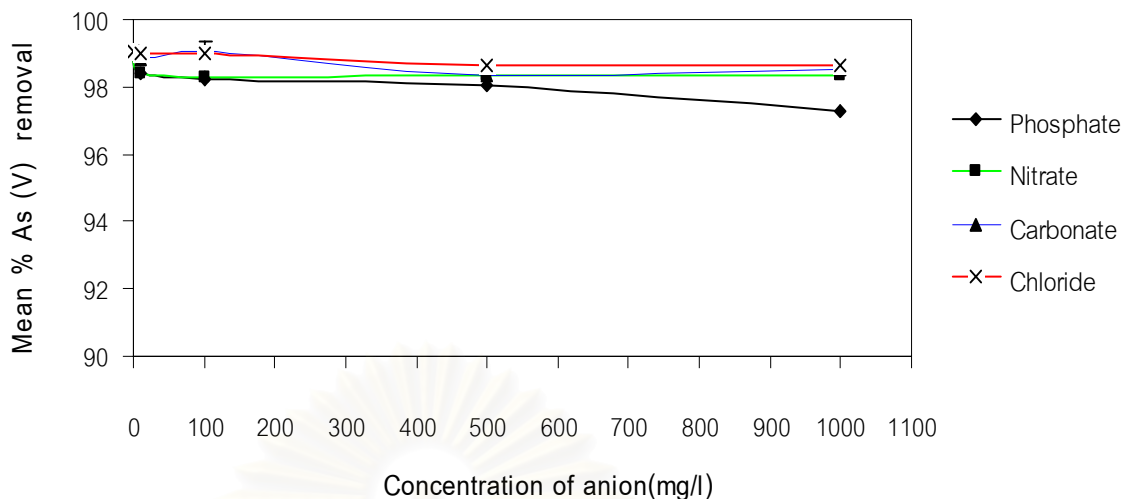
Figure 4.17 The comparison of the effect of anions on As (V) removal by CD4006 adsorbent

The comparison of the effect of each anions on As (V) removal were shown in Figure 4.16.It was observed that in the presence of the concentration between 10 to 1000mg/l of anions, chloride, carbonate and nitrate had a little effect on As(V) removal. In addition, phosphate alone had a significant effect on As (V) removal when the concentration of phosphate increased to 1000 mg/l because phosphate ion was chemically similar to arsenate and may substituted at the adsorption site on the surface of CD8006. According to the result of Meng et al. (2003) who studied the effect of sulfate, carbonate and silicate on the removal of As (III) and As (V) removal by using ferric chloride as adsorbent. They found that sulfate and carbonate had a negligible effect on the removal of As (III) and As (V). Xu et al.(2002) reported that the addition of chloride, nitrate and acetate ions at 1mg/l had affected the As(V) adsorption, whereas the existing phosphate and sulfate could significantly reduce the removal of As(V) by aluminum-loaded zeolite.

4.5.3 The effects of mixing competing anions on the efficiency of CD4006 adsorbent for As (III) removal and CD8006 for As (V) removal

The effects of mixing anions on As (III) and As (V) removal were evaluated in arsenic – spike water. Phosphate, nitrate, carbonate and chloride were

combined in the concentration of 100 mg/l and added into the solution. The optimum conditions for this studied was as follows: pH 5, contact time 300 min. and the 3.0 g CD4006 adsorbent for As (III) removal and 3.0 g CD8006 adsorbent. The results of experimental were shown in appendix C, TableC.10.

The results from this studied were shown in Table 4.13 and Figure 4.17. It was found that at concentration of 100 mg/l the percentage removal of As (III) and As (V) were 97.28%, and 99.05%, respectively. In Figure 4.17 it was observed that the presence of 100 mg/l of combined anions was not affected to As (V) removal whereas little slightly affected to decrease As (III) removal. From statistical analysis, it was shown those combined anions: nitrate, carbonate and chloride were not significant difference between treatments at 95% confident level. The results of statistical analysis were shown in appendix B, Table B.11

In this experiment, it should be noted that the mixing competing anions were not affected on the efficiency of CD4006 adsorbent for As (III) removal and CD8006 for As (V) removal.

Table 4.13 The effect of mixing competing anions on As (III) and As (V) removal by CD 4006 and CD 8006

Concentration of mixing anions (mg/l)	Arsenic removal (%)	
	As (III)	As (V)
0	98.77±0.14 [a]	99.05±0.07 [a]
100	97.28±0.07 [a]	99.05±0.07 [a]

Note: The same alphabet on the top of right corner in each row meaned there was no significant difference at 95% confident level
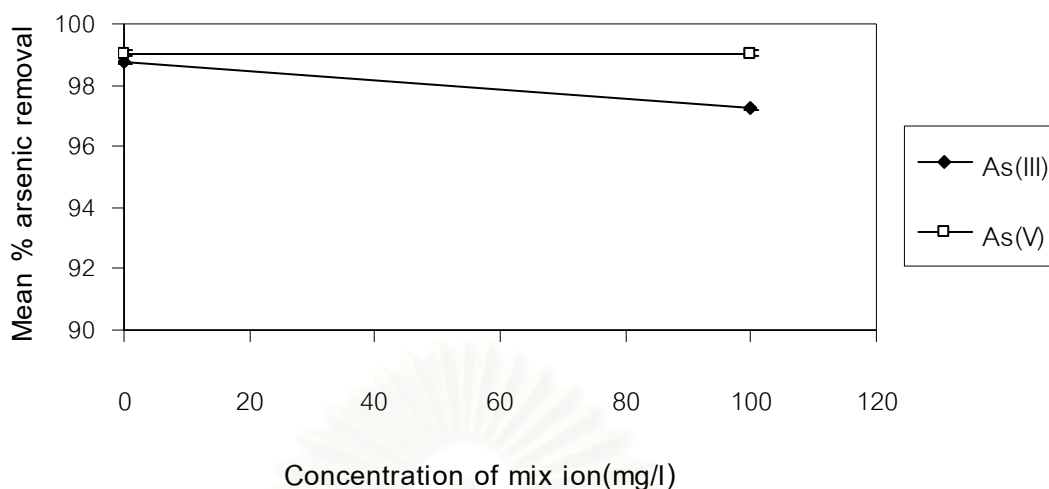
Figure 4.17 Comparison of percentage removal of As (III) and As (V) at concentration of mix ion 100mg/l by CD 4006 and CD 8006

4.6 The efficiency of CD4006 and CD8006 adsorbent in removal arsenic from arsenic contaminated surface water

4.6.1 Water quality of sample

The water sample was obtained from Faculty of Environmental Engineering Kasetsart University which collected from the stream in Moo 1 Ron Pibun district Nakorn Si Tammarat province. It was determined pH, suspended solids and concentration of arsenic. The result was shown in Table 4.16.

Table 4.14 Water quality parameters of arsenic contaminated surface water

Parameter	pH	SS (mg/l)	As (mg/l)
arsenic contaminated surface water	2.45 *	42	1.95

* Preserved with hydrochloric acid

4.6.2 Treatment with CD4006 and CD8006 adsorbent

The arsenic contaminated surface water was treated using diatomite adsorbent: CD4006 andCD8006 at the amount of 0.1, 0.5, 1 and 2 g, respectively. The optimum conditions were conducted at pH 5, contact time 300 min. The results of experimental were shown in appendix C, TableC.13.

The arsenic removal efficiency as a function of the amount of adsorbent was shown in Figure 4.18
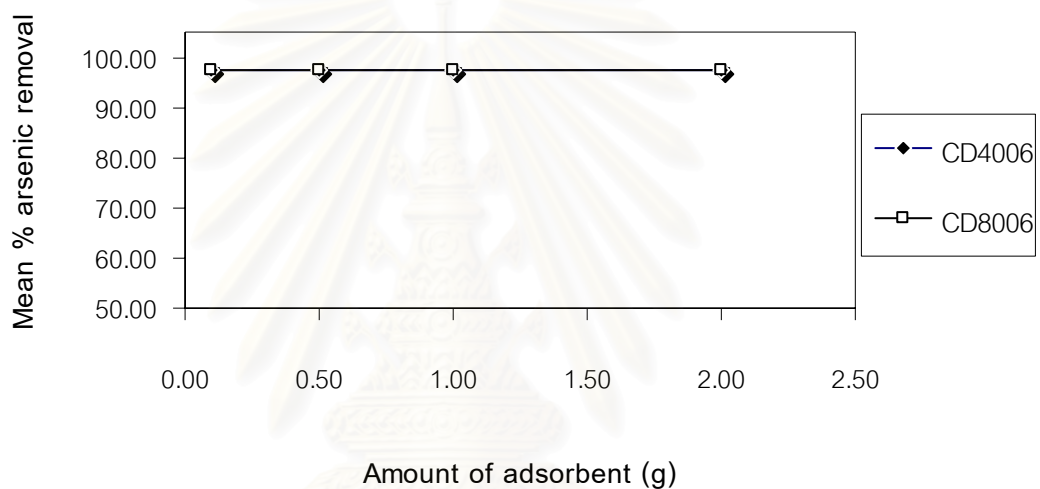
Figure 4.18 The arsenic removal efficiency with various adsorbent dosages (50 ml, pH 5, contact time 5 hrs)

As shown in Figure 4.18, CD4006 adsorbent and CD8006 adsorbent had a similar removal pattern with the percentage removal were > 97.42%. From experiment it found that in arsenic contaminated surface water the adsorption capacity of both CD4006 adsorbent and CD8006 adsorbent were 9.8 mgAs/g.

4.6.3 Water quality after treatment

The water qualities after treatment were summarized in Table 4.17.According to this results it was found that 0.1 g of CD4006 andCD8006 adsorbents could reduced the concentration of arsenic from 1.95 mg/l to below the regulatory limits

of WHO Bottled Drinking Water Standards (2001) (maximum allowable 0.01 mg/l). This suggested that water quality after As treatment with   CD4006 andCD8006 adsorbents could meet the discharge standards and could dispose to environment.

Table 4.15 The water qualities after treatment with CD4006 and CD8006

Adsorbent	pH (after)	Amount (g)	As remained(mg/l)	Percentage removal (%)
CD4006	4.73	0.1	<0.05	> 97.42
CD8006	4.75	0.1	<0.05	> 97.42

Arsenic impregnated calcined diatomite could be disposed in a hazardous waste landfill. The cost of disposal of the spent calcined diatomite would also have to consider in any detailed economic analysis required to determine the most economical adsorbent.

The cost of the adsorbent was also one important that must be considered when selecting an adsorbent. The cost of commercial activated carbon was 5 – 6 USD per kg (approximately), whereas the cost of diatomite is less than 1 USD per kg. The regeneration and reuse of calcined diatomite may play an important role in the practical process.

According to the experimental results of this study. CD4006 adsorbent and CD8006 adsorbent can be considered as an alternative material to remove arsenic from arsenic contaminated water due to high efficiency, low cost and availability from natural resources.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The following conclusions can be presented from the experimental results;

1) The removal efficiency of As(III) and As(V) using diatomite quality improvement by calcination were depended on the temperature of calcination in ranges from 200°C to 800°C but were not depended on the time of calcination in ranges from 2 hrs to 8 hrs. From the batch studied, it can be observed that the optimum adsorbent for As (III) removal was calcined diatomite adsorbent at $400\ ^{\circ}$C for 6 hrs (CD4006) and the optimum adsorbent for As (V) removal was calcined diatomite adsorbent at $800\ ^{\circ}$C for 6 hrs (CD8006).

2) From the physical properties studied, it can be observed that before calcination, Lampang diatomite was yellowish – brown and looked like fine powder after calcination the colour of CD4006 and CD8006 became reddish – brown and dark reddish brown. The specific surface area of Lampang diatomite was 65.73 m^2/g. After calcination at $400\ ^{\circ}$C for 6 hrs the specific surface area was increased to 66.07 m^2/g. In contrast, the specific surface area was decreased to 60.97 m^2/g after calcination at $800\ ^{\circ}$C for 6 hrs.

3) From the chemical composition studied, it can be observed that the mainly chemical composition of Lampang diatomite was SiO_2 79.61 %, Al_2O_3 11.86% and Fe_2O_3 3.83%. Calcined diatomite (CD4006) was mainly of 76.48% SiO_2, 7.58% Al_2O_3 and 6.01%Fe_2O_3 while the chemical composition of calcined diatomite (CD8006) was SiO_2 79.04 %, Al_2O_3 7.96% and Fe_2O_3 6.26%.

4) From the batch studied, it can be observed that the As (III) and As (V) removal were found to depend on pH, contact time and adsorbent dose whereas the concentration was independent.

5) The maximum of 98.72% As (III) removal by CD4006 and 99.05% As (V) removal by CD8006 can be achieved at optimum conditions: the concentrations of 10 mg/l, pH 5, contact time 300 min and dose of adsorbent 3.0 g.

6) The adsorption isotherm test of As(III) and As(V) indicated that the adsorption pattern for As (III) and As (V) on CD4006 and CD8006 followed the Freundlich isotherm.

7) The presence of phosphate at the concentration of 100 mg/l was found to be effect on As (III) and As(V) removal and the other anions were not effect on As(III) and As(V) removal.

8)   The comparison CD4006 adsorbent and CD8006 adsorbent using for arsenic contaminated surface water removal are shown high removal efficiency > 95% and residue concentration of arsenic contaminated surface water are within the WHO (< 0.05 mg/l). The adsorption capacity of both CD4006 adsorbent and CD8006 adsorbent were 9.8 mgAs/g.

5.2 Recommendations

Recommendations for future studies and research are as follows;

1) A similar study should be conducted to use CD8006 adsorbent for removal arsenic in natural petroleum.

2)   The adsorbent particle size is one of the parameter which affects the adsorption process. In this studied the particle size of adsorbent is fixed, so it should be varied with different particle sizes in further study.

3)   A similar study should be conducted in continuous process such as fixed bed in order to study the lifetime of adsorbent.

4)   The spent calcined diatomite adsorbent waste is concerned, it has been found useful as material for making brick and road construction.

5)   The regeneration and reuse of calcined diatomite adsorbent is not considered in this study. However, a further study would be useful.

6) The studies of the other factors affecting the adsorption performance such as the presence of BOD, COD, suspended solid, nutrients, silica or mica in the wastewater should be considered for further study.

7) A similar study should be conducted to use CD8006 in the removal of arsenic from agricultural wastewater or industrial wastewater.

8) Due to phosphate ion affect to the performance of CD 4006 and CD8006 for removal As (III) and As (V) .It should be treated before using these adsorbents in adsorption process.

9) CD4006 and CD8006 adsorbents may be used as polishing step for other water treatment technologies.

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APPENDICES

Appendix A

ASTM-D4309-02

Standard Practice for Sample Digestion Using Closed Vessel Microwave Heating

Technique for the Determine of Total Metals in Water

1.   **Scope**

1.1   This practice covers the general consideration for quantitative sample digestion for total metals in water using closed vessel microwave heating technique. This practice is applicable to surface, saline, domestic, and industrial wastewater.

1.2   Because of the differences among various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument.

2.   **Summary of Practice**

A representation aliquot of a homogeneous sample is digested with acid in a closed microwave transparent vessel, using microwave heating. The digestate or a filtered digestate is then analyzed by direct aspiration or injection by flame atomic absorption spectrophotometry (FAAS), inductively coupled plasma emission techniques (ICP), Direct current plasma emission techniques (DCP), or graphite furnace atomic absorption spectrophotometry (GFAAS), or a combination of methods.

3.   **Significant and use**

The analysis of many types of water for metals using flame atomic absorption spectrophotometry, inductively coupled plasma emission spectrophotometry, direct current plasma emission spectrophotometry, or graphite furnace atomic absorption spectrophotometry necessitates the use of a digestion practice in order to ensure the proper statistical recovery of the metals from the sample matrix. The use of closed

vessel microwave techniques will speed the complete sample contamination from external sources.

4.   Interference

4.1   No interference have been observed using microwave heating

4.2   Precautions should be exercised to avoid those interference's normally associated with the particular analytical method for metals determination.

4.3   This practice will not totally solubilize solid silicates that are suspended in of settle out of the water sample.

5.   Apparatus

5.1   Laboratory Microwave Heating System, capable of delivering 575 to 1000 W of power. The unit should be capable of 1% power adjustment and 1 s time adjustment. The oven cavity should be capable of 1% power adjustment and 1 s time adjustment. The oven cavity should be fluorocarbon-coated or coated with a material that has equivalent acid resistance and microwave properties and be equipped with exhaust ventilation at 2.8 m^3/min (100 ft^3/min) for acid vapor protection of the unit and operator. The unit must have a rotating or alternating turntable, capable of holding 1 to 14 digestion vessels, to ensure even sample heating. Safety interlocks, to shut off magnetron power output, must be contained in the oven door opening mechanism. The unit may contain a temperature control device capable of controlling vessel temperatures to 200°C and/or a pressure control device capable of controlling vessel pressures to a minimum 100 psig.

5.2   Closed Vessels, capable of holding 100 mL of solution. The vessel must be transparent to microwave energy and capable of withstanding internal pressures of 100 psig and temperatures of 200 ^{o}C. The vessel must contain a safety pressure relief valve, rupture disc, pressure venting system or be connected to an external safety relief valve that will prevent possible vessel rupture or ejection of the vessel cap.

5.3   Apparatus, to seal the vessel system to the manufacturer's specified requirement.

6.   **Reagents**

6.1   Hydrochloric Acid (sp gr 1.19) (HCl).

6.2   Nitric acid, 70%, (sp gr 1.42) (HNO_3).

6.3   Nitric acid (1+1) Add 1 volume of HNO_3 (sp gr 1.42) to 1 volume of water.

7.   **Hazards**

7.1   The microwave unit should be operated in accordance with the manufacturer's recommended operating and safety precautions. Caution-It is not recommended to place a microwave unit in a fume hood, where it is surrounded by acid fumes, which can cause corrosion of the equipment. Acid fumes generated inside the oven cavity should be air swept away from the oven cavity to a hood.

7.2   Precaution-The closed vessel should be operated in accordance with the manufacturer's recommended operating and safety instructions.

8.   **Procedure**

8.1   Power Temperature Control-procedure for 1 to 14 vessel digestions:

8.1.1   Transfer 50.0 mL of a representative aliquot of the well-mixed sample into a clean vessel (see Note 2). If the sample is to be analyzed by ICP, DCP, or FAAS, add 3 mL of HNO_3 (sp gr 1.42) and 2 mL of HCL (sp gr 1.19). If the sample is to be analyzed by GFAAS, add 5 mL HNO_3 (sp gr 1.42) (see Note 3). Install a safety pressure relief valve and cap on the vessel and seal to the manufacturer's recommended toque. Weigh the sealed container, record the weight, and if required, complete the assembly of the vessel and place in the microwave instrument turntable following the manufacturer's operating instructions.

Note 2 – Follow the manufacturer's suggested vessel cleaning instructions to avoid possible sample contamination.

Note 3 – Final acid concentration of this procedure is 9%. This may shorten graphite tube lifetime, which may cause deterioration of analyst recovery. The analyst may choose to dilute the digested solution to a lower acid percentage to increase graphite tube life.

8.1.2   Repeat 8.1.1 until the turntable contains from 1 to 14 symmetrically spaced vessels, one of which is a temperature control vessel. This will insure even heating of all vessels. A reagent blank should be digested and analyzed along with the samples.

8.1.3   Program the instrument to reach $170^{\circ}C$ in 20 minutes and maintain that temperature for 10 minutes. Depress the start key and allow the sample mixtures to heat for programmed times.

8.1.4   At the end of the digestion period, remove the vessels from the microwave and allow the sample solutions to cool to room temperature. Shake the vessels to mix the sample solutions and vent to atmosphere any gas pressure that may be present in the vessels.

8.1.5   Remove the vessel assembly from the turntable. Weigh the cooled vessel system. If there is a weight loss greater than 0.5 g, open the vessel and add an amount of reagent water equal to the weight loss (see Note 6). Recap the vessel and then shake the vessel to mix the sample solution. Liquid loss of less than 10 % has not been found to result in analyte loss.

Note 6 – Samples containing large amounts of organic any experience excessive loss of liquid (greater than 10%); therefore a study may be required to determine if any analyte loss occurred.

8.1.6   Open the vessel and filter the samples, if required, to remove silicates and other insoluble materials. Do not rinse or dilute the digested sample. Final sample volume is 55 mL (see Note 3 and Note 7).

Note 7 – In place of filtering, the sample after mixing may be centrifuge or allowed to settle by gravity overnight to remove insoluble material.

8.1.7   Analyze the sample solution by ICP - OES, ICP – MS, DCP, FAAS or GFAAS, or combination of methods required.

9.   Calculation

The analyst is to refer to the specific standard test method for either ICP, DCP, or FAAS, or GFAAS, or combination of methods. The standard test methods contain all the information for constructing calibration curves and calculations necessary for the determination of the metal concentrations on the water matrices under which they were tested.

10.   Precision and Bias

10.1   Precision – This practice was tested by digesting different samples of NPDES effluent water by one laboratory Table X1.1 contains element concentration recovery conducted on four portions of the samples digested by this practice and by EPA Digestion Procedure 4.1.3. All Element concentrations were determined by inductively coupled plasma spectroscopy techniques.

10.2   Precision and bias for the standards listed in 1.3 were determined using the total recoverable metals digestion procedures included in those standards and are not

applicable to this practice. It is the responsibility of the user to establish the precision and bias of the digestion practice in conjunction with the analytical measuring method.

11.   **Keywords**

Digestion; metals; microwave; vessel

APPENDIX B

STATISTICAL ANALYSIS

B-1 Test of calcination temperature on arsenic removal

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
As_III_ removal	Between Groups	1291.226	4	322.806	161.044	.000
	Within Groups	10.022	5	2.004		
	Total	1301.248	9			
As_V_ removal	Between Groups	1736.446	4	434.112	1793.849	.000
	Within Groups	1.210	5	.242		
	Total	1737.656	9			

Post Hoc Tests

Homogeneous Subsets

As_III_removal

Duncan[a]

		Subset for alpha = .05				
Temp_T_	N	1	2	3	4	5
800.00	2	49.2300				
600.00	2		63.1450			
.00	2			70.1000		
200.00	2				76.0300	
400.00	2					82.1750
Sig.		1.000	1.000	1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed.
 a. Uses Harmonic Mean Sample Size = 2.000.

As_V_removal

Duncan[a]

		Subset for alpha = .05			
Temp_T_	N	1	2	3	4
600.00	2	55.2000			
400.00	2	56.3500	56.3500		
.00	2		56.5500		
200.00	2			63.0000	
800.00	2				90.0000
Sig.		.067	.701	1.000	1.000

Means for groups in homogeneous subsets are displayed.
 a. Uses Harmonic Mean Sample Size = 2.000.

B-2 Test of calcination time on arsenic removal

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
As_III_removal	Between Groups	16.445	3	5.482	4.774	.083
	Within Groups	4.593	4	1.148		
	Total	21.038	7			
As_V_removal	Between Groups	2.020	3	.673	7.481	.041
	Within Groups	.360	4	.090		
	Total	2.380	7			

Post Hoc Tests

Homogeneous Subsets

As_III_removal

Duncan[a]

Time_Hr_	N	Subset for alpha = .05	
		1	2
8.00	2	78.3500	
4.00	2	79.1250	
2.00	2	79.6400	79.6400
6.00	2		82.1750
Sig.		.301	.077

Means for groups in homogeneous subsets are displayed.
a. Uses Harmonic Mean Sample Size = 2.000.

As_V_removal

Duncan[a]

Time_Hr_	N	Subset for alpha = .05	
		1	2
8.00	2	88.7000	
2.00	2	88.9000	
4.00	2	89.4000	89.4000
6.00	2		90.0000
Sig.		.084	.116

Means for groups in homogeneous subsets are displayed.
a. Uses Harmonic Mean Sample Size = 2.000.

B-3 Test of concentration on As(III) and As(V) removal

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
As_III_ removal	Between Groups	38.460	4	9.615	2.153	.211
	Within Groups	22.325	5	4.465		
	Total	60.785	9			
As_V_ removal	Between Groups	28.674	4	7.169	2.798	.145
	Within Groups	12.810	5	2.562		
	Total	41.484	9			

Post Hoc Tests

Homogeneous Subsets

As_III_removal

Duncan[a]

Concentration	N	Subset for alpha = .05 1
.50	2	79.0000
1.00	2	81.0000
2.00	2	82.0000
5.00	2	83.8000
10.00	2	84.4500
Sig.		.057

Means for groups in homogeneous subsets are displayed.
  a. Uses Harmonic Mean Sample Size = 2.000.

As_V_removal

Duncan[a]

Concentration	N	Subset for alpha = .05 1
.50	2	86.0000
1.00	2	86.5000
2.00	2	88.7500
5.00	2	89.9000
10.00	2	90.0500
Sig.		.060

Means for groups in homogeneous subsets are displayed.
  a. Uses Harmonic Mean Sample Size = 2.000.

B-4 Test of pH on As(III) and As(V) removal

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
As_III_ removal	Between Groups	21.064	5	4.213	69.383	.000
	Within Groups	.364	6	.061		
	Total	21.428	11			
As_V_ removal	Between Groups	.568	5	.114	2.308	.169
	Within Groups	.295	6	.049		
	Total	.863	11			

Post Hoc Tests

Homogeneous Subsets

As_III_removal

Duncan[a]

		Subset for alpha = .05		
pH	N	1	2	3
9.00	2	81.0450		
8.00	2		83.0950	
7.00	2		83.1950	
6.00	2		83.2450	
4.00	2			84.7350
5.00	2			85.1450
Sig.		1.000	.577	.147

Means for groups in homogeneous subsets are displayed.
a. Uses Harmonic Mean Sample Size = 2.000.

As_V_removal

Duncan[a]

		Subset for alpha = .05	
pH	N	1	2
9.00	2	89.3000	
8.00	2	89.4500	89.4500
6.00	2	89.6500	89.6500
7.00	2	89.6500	89.6500
4.00	2	89.7000	89.7000
5.00	2		90.0000
Sig.		.138	.058

Means for groups in homogeneous subsets are displayed.
a. Uses Harmonic Mean Sample Size = 2.000.

B-5 Test of contact time on As(III) and As(V) removal

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
As_III_ removal	Between Groups	12.064	9	1.340	49.236	.000
	Within Groups	.272	10	.027		
	Total	12.336	19			
As_V_ removal	Between Groups	4.025	9	.447	9.220	.001
	Within Groups	.485	10	.049		
	Total	4.510	19			

Post Hoc Tests

Homogeneous Subsets

As_III_removal

Duncan[a]

		Subset for alpha = .05					
Time	N	1	2	3	4	5	6
30.00	2	84.5300					
60.00	2		84.9400				
120.00	2		85.0450				
90.00	2		85.1450				
150.00	2			85.9650			
180.00	2			86.1700	86.1700		
240.00	2				86.3750	86.3750	
300.00	2					86.5800	86.5800
360.00	2					86.5800	86.5800
420.00	2						86.7850
Sig.		1.000	.263	.242	.242	.263	.263

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 2.000.

As_V_removal

Duncan[a]

		Subset for alpha = .05		
Time	N	1	2	3
30.00	2	89.9500		
60.00	2	90.2000	90.2000	
150.00	2	90.4000	90.4000	
90.00	2		90.5000	
120.00	2		90.5000	
180.00	2		90.6000	
420.00	2			91.1000
240.00	2			91.2000
360.00	2			91.2000
300.00	2			91.3000
Sig.		.079	.126	.416

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 2.000.

B-6 Test of amount of adsorbent on As(III) and As(V) removal

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
As_III_removal	Between Groups	1324.634	5	264.927	6229.909	.000
	Within Groups	.255	6	.043		
	Total	1324.890	11			
As_V_removal	Between Groups	1249.158	5	249.832	14276.086	.000
	Within Groups	.105	6	.018		
	Total	1249.263	11			

Post Hoc Tests

Homogeneous Subsets

As_III_removal

Duncan[a]

		Subset for alpha = .05			
Amount_g_	N	1	2	3	4
.10	2	69.2650			
.50	2		86.3750		
1.00	2			93.4450	
2.00	2				96.6200
3.00	2				
4.00	2				
Sig.		1.000	1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed.

As_III_removal

Duncan[a]

	Subset for alpha = .05	
Amount_g_	5	6
.10		
.50		
1.00		
2.00		
3.00	98.7200	
4.00		99.4900
Sig.	1.000	1.000

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 2.000.

As_V_removal

Duncan[a]

Amount_g_	N	Subset for alpha = .05			
		1	2	3	4
.10	2	70.3000			
.50	2		91.8000		
1.00	2			95.1000	
2.00	2				98.1000
3.00	2				
4.00	2				
Sig.		1.000	1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed.

As_V_removal

Duncan[a]

Amount_g_	Subset for alpha = .05	
	5	6
.10		
.50		
1.00		
2.00		
3.00	99.0500	
4.00		99.6000
Sig.	1.000	1.000

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 2.000.

B-7 Test of phosphate concentration on As(III) and As(V) removal

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
As_III_ removal	Between Groups	26.259	4	6.565	79.236	.000
	Within Groups	.414	5	.083		
	Total	26.673	9			
As_V_ removal	Between Groups	3.190	4	.798	56.964	.000
	Within Groups	.070	5	.014		
	Total	3.260	9			

Post Hoc Tests

Homogeneous Subsets

As_III_removal

Duncan[a]

		Subset for alpha = .05		
Phosphate_conc_	N	1	2	3
1000.00	2	94.4150		
500.00	2	94.7200		
100.00	2	94.9800		
10.00	2		96.5700	
.00	2			98.7700
Sig.		.115	1.000	1.000

Means for groups in homogeneous subsets are displayed.
  a. Uses Harmonic Mean Sample Size = 2.000.

As_V_removal

Duncan[a]

		Subset for alpha = .05			
Phosphate_conc_	N	1	2	3	4
1000.00	2	97.3000			
500.00	2		98.0500		
100.00	2		98.2000	98.2000	
10.00	2			98.4000	
.00	2				99.0500
Sig.		1.000	.261	.152	1.000

Means for groups in homogeneous subsets are displayed.
  a. Uses Harmonic Mean Sample Size = 2.000.

B-8 Test of nitrate concentration on As(III) and As(V) removal

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
As_III_ removal	Between Groups	1.828	4	.457	38.621	.001
	Within Groups	.059	5	.012		
	Total	1.887	9			
As_V_ removal	Between Groups	.794	4	.199	28.357	.001
	Within Groups	.035	5	.007		
	Total	.829	9			

Post Hoc Tests

Homogeneous Subsets

As_III_removal

Duncan[a]

Nitrate_conc_	N	Subset for alpha = .05	
		1	2
100.00	2	97.6450	
10.00	2	97.6950	
500.00	2	97.6950	
1000.00	2	97.8000	
.00	2		98.7700
Sig.		.226	1.000

Means for groups in homogeneous subsets are displayed.
   a. Uses Harmonic Mean Sample Size = 2.000.

As_V_removal

Duncan[a]

Nitrate_conc_	N	Subset for alpha = .05	
		1	2
100.00	2	98.3000	
500.00	2	98.3500	
1000.00	2	98.3500	
10.00	2	98.4000	
.00	2		99.0500
Sig.		.299	1.000

Means for groups in homogeneous subsets are displayed.
   a. Uses Harmonic Mean Sample Size = 2.000.

B-9 Test of carbonate concentration on As(III) and As(V) removal

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
As_III_ removal	Between Groups	3.252	4	.813	45.110	.000
	Within Groups	.090	5	.018		
	Total	3.342	9			
As_V_ removal	Between Groups	.566	4	.142	6.152	.036
	Within Groups	.115	5	.023		
	Total	.681	9			

Post Hoc Tests

Homogeneous Subsets

As_III_removal

Duncan[a]

		Subset for alpha = .05	
Carbonate_conc_	N	1	2
10.00	2	97.2850	
1000.00	2	97.3350	
100.00	2	97.3400	
500.00	2	97.4400	
.00	2		98.7700
Sig.		.313	1.000

Means for groups in homogeneous subsets are displayed.
  a. Uses Harmonic Mean Sample Size = 2.000.

As_V_removal

Duncan[a]

		Subset for alpha = .05		
Carbonate_conc_	N	1	2	3
500.00	2	98.3500		
1000.00	2	98.5500	98.5500	
100.00	2	98.6000	98.6000	
10.00	2		98.8000	98.8000
.00	2			99.0500
Sig.		.170	.170	.160

Means for groups in homogeneous subsets are displayed.
  a. Uses Harmonic Mean Sample Size = 2.000.

B-10 Test of chloride concentration on As(III) and As(V) removal

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
As_III_ removal	Between Groups	3.134	4	.783	69.884	.000
	Within Groups	.056	5	.011		
	Total	3.190	9			
As_V_ removal	Between Groups	.326	4	.082	4.289	.071
	Within Groups	.095	5	.019		
	Total	.421	9			

Post Hoc Tests

Homogeneous Subsets

As_III_removal

Duncan[a]

		Subset for alpha = .05	
Chloride_conc_	N	1	2
100.00	2	97.2850	
10.00	2	97.3900	
1000.00	2	97.3900	
500.00	2	97.4400	
.00	2		98.7700
Sig.		.216	1.000

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 2.000.

As_V_removal

Duncan[a]

		Subset for alpha = .05	
Chloride_conc_	N	1	2
500.00	2	98.6500	
1000.00	2	98.6500	
10.00	2	99.0000	99.0000
100.00	2	99.0000	99.0000
.00	2		99.0500
Sig.		.059	.737

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 2.000.

B - 11 Test of mix ion concentration on As (III) and As (V) removal

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	MIX_ION & AS_III_R	4	-.994	.006
Pair 2	MIX_ION & AS_V_REM	4	.000	1.000

Paired Samples Test

		Paired Differences		
		Mean	Std. Deviation	Std. Error Mean
Pair 1	MIX_ION - AS_III_R	-48.0275	58.59247	29.29623
Pair 2	MIX_ION - AS_V_REM	-49.0500	57.73506	28.86753

Paired Samples Test

		Paired Differences	
		95% Confidence Interval of the Difference	
		Lower	Upper
Pair 1	MIX_ION - AS_III_R	-141.2612	45.2062
Pair 2	MIX_ION - AS_V_REM	-140.9194	42.8194

Paired Samples Test

		t	df	Sig. (2-tailed)
Pair 1	MIX_ION - AS_III_R	-1.639	3	.200
Pair 2	MIX_ION - AS_V_REM	-1.699	3	.188

APPENDIX C

Table C.1 Data of percentage As(III) and As(V)removal by diatomite and calcined diatomite (CD) at different temperature and time
(Shaking time = 120 minutes,pH =7,0.5 g adsorbent,50 ml)

Experiment No.		Adsorbent		pH As(III)		pH As(V)		Co(mg/l)		Ce(mg/l)		% removal		Ave.% removal		SD. % removal	
		As(III)	As(V)	Before	After	Before	After	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
1	1	Control	Control	7.10	5.62	6.95	5.32	9.76	10.00	2.82	4.34	71.13	56.60	70.10	56.55	1.46	0.07
	2			7.09	6.65	6.96	5.30	9.76	10.00	3.02	4.35	69.07	56.50				
2	1	CD 2002	CD 2002	7.12	5.62	7.06	5.52	9.76	10.00	2.77	3.96	71.65	60.40	72.17	60.55	0.73	0.21
	2			7.08	5.65	7.06	5.62	9.76	10.00	2.67	3.93	72.68	60.70				
3	1	CD 2004	CD 2004	7.10	5.55	7.00	5.55	9.76	10.00	2.16	4.00	77.84	60.00	76.81	59.85	1.46	0.21
	2			7.05	5.60	7.06	5.40	9.76	10.00	2.36	4.03	75.77	59.70				
4	1	CD 2006	CD 2006	7.02	5.51	7.01	5.11	9.76	10.00	2.41	3.71	75.26	62.90	76.03	63.00	1.09	0.14
	2			7.02	5.50	6.93	5.19	9.76	10.00	2.26	3.69	76.80	63.10				
5	1	CD 2008	CD 2008	7.00	5.43	6.96	5.13	9.76	10.00	2.47	4.12	74.74	58.80	73.71	58.85	1.46	0.07
	2			7.00	5.42	7.03	5.14	9.76	10.00	2.67	4.11	72.68	58.90				
6	1	CD 4002	CD 4002	7.02	5.45	7.03	5.27	9.76	10.00	1.91	3.83	80.41	61.70	79.64	61.85	1.09	0.21
	2			6.99	5.43	7.03	5.20	9.76	10.00	2.06	3.80	78.87	62.00				
7	1	CD 4004	CD 4004	7.05	5.49	7.07	5.32	9.76	10.00	1.96	4.07	79.90	59.30	79.13	59.50	1.10	0.28
	2			7.05	5.49	7.10	5.30	9.76	10.00	2.11	4.03	78.35	59.70				
8	1	CD 4006	CD 4006	7.00	5.48	7.09	5.62	9.76	10.00	1.76	4.39	81.97	56.10	82.17	56.35	0.29	0.35
	2			6.95	5.50	7.06	5.63	9.76	10.00	1.72	4.34	82.38	56.60				
9	1	CD 4008	CD 4008	7.09	5.52	7.10	5.13	9.76	10.00	2.01	4.23	79.38	57.70	78.35	57.55	1.46	0.21
	2			7.06	5.51	7.12	5.12	9.76	10.00	2.21	4.26	77.32	57.40				

Table C.1 (continue)   Data of percentage As(III) and As(V)removal   by diatomite and calcined diatomite (CD) at different temperature and time
(Shaking time = 120 minutes,pH =7,0.5 g adsorbent,50 ml)

Experiment No.		Adsorbent		pH As(III)		pH As(V)		Co(mg/l)		Ce(mg/l)		% removal		Ave.% removal		SD. % removal	
		As(III)	As(V)	Before	After	Before	After	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
10	1	CD 6002	CD 6002	7.03	5.57	7.09	5.18	9.76	10.00	3.52	4.42	63.92	55.80	62.63	55.60	1.82	0.28
	2			7.07	5.65	7.06	5.18	9.76	10.00	3.77	4.46	61.34	55.40				
11	1	CD 6004	CD 6004	7.06	5.69	7.00	5.13	9.76	10.00	3.97	4.60	59.28	54.00	60.31	53.95	1.46	0.07
	2			7.06	5.70	7.10	5.12	9.76	10.00	3.77	4.61	61.34	53.90				
12	1	CD 6006	CD 6006	7.08	5.58	7.02	5.15	9.76	10.00	3.72	4.41	61.86	55.90	63.15	55.20	1.82	0.99
	2			7.09	5.55	7.04	5.17	9.76	10.00	3.47	4.55	64.43	54.50				
13	1	CD 6008	CD 6008	7.05	5.66	7.09	5.23	9.76	10.00	3.87	4.82	60.31	51.80	61.60	51.95	1.82	0.21
	2			7.05	5.69	7.07	5.22	9.76	10.00	3.62	4.79	62.89	52.10				
14	1	CD 8002	CD 8002	7.10	5.64	7.03	5.65	9.76	10.00	4.78	1.12	51.03	88.80	49.23	88.90	2.55	0.14
	2			7.06	5.62	7.03	5.70	9.76	10.00	5.13	1.10	47.42	89.00				
15	1	CD 8004	CD 8004	7.08	5.62	7.05	5.73	9.76	10.00	5.23	1.04	46.39	89.60	47.94	89.40	2.18	0.28
	2			7.00	5.62	7.01	5.75	9.76	10.00	4.93	1.08	49.48	89.20				
16	1	CD 8006	CD 8006	6.95	5.64	7.10	5.90	9.76	10.00	5.08	0.98	47.94	90.20	49.23	90.00	1.82	0.28
	2			7.01	5.64	7.12	5.92	9.76	10.00	4.83	1.02	50.52	89.80				
17	1	CD 8008	CD 8008	6.98	5.65	7.01	5.82	9.76	10.00	4.98	1.10	48.97	89.00	47.17	88.70	2.55	0.42
	2			7.05	5.58	7.07	5.78	9.76	10.00	5.33	1.16	45.36	88.40				

TableC.2 Data of percentage As(III) andAs(V) removal by calcined diatomite(CD4006) and (CD 8006) at different concentration (Shaking time = 120 minutes,pH =7 0.5 g adsorbent,50 ml)

Experiment No.		Adsorbent		pH As(III)		pH As(V)		Co(mg/l)		Ce(mg/l)		%removal		Ave.%removal		SD.%removal	
		As(III)	As(V)	Before	After	Before	After	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
0	1	CD 4006	CD 8006	7.10	6.10	6.95	5.87	0.02	0.02	0.02	0.02	0.00	0.00	0.00	0.00	0.00	0.00
	2			7.12	6.02	6.99	5.75	0.02	0.02	0.02	0.02	0.00	0.00				
1	1	CD 4006	CD 8006	7.06	5.75	6.94	5.87	0.50	0.50	0.09	0.08	82.00	84.00	79.00	86.00	4.24	2.83
	2			7.02	5.74	6.98	5.73	0.50	0.50	0.12	0.06	76.00	88.00				
2	1	CD 4006	CD 8006	7.05	5.62	6.96	5.87	1.00	1.00	0.18	0.12	82.00	88.00	81.00	86.50	1.41	2.12
	2			7.05	5.63	6.98	5.75	1.00	1.00	0.2	0.15	80.00	85.00				
3	1	CD 4006	CD 8006	7.01	5.52	7.08	5.73	2.00	2.00	0.38	0.22	81.00	89.00	82.00	88.75	1.41	0.35
	2			6.93	5.54	7.10	5.78	2.00	2.00	0.34	0.23	83.00	88.50				
4	1	CD 4006	CD 8006	7.08	5.48	7.05	5.74	5.00	5.00	0.83	0.49	83.40	90.20	83.80	89.90	0.57	0.42
	2			7.09	5.55	7.08	5.78	5.00	5.00	0.79	0.52	84.20	89.60				
5	1	CD 4006	CD 8006	6.99	5.49	7.10	5.77	10.00	10.00	1.56	1.00	84.40	90.00	84.45	90.05	0.07	0.07
	2			7.00	5.53	7.12	5.72	10.00	10.00	1.55	0.99	84.50	90.10				

Table C.3 Data of percentage As(III) andAs(V) removal by diatomite(CD4006) adsorbent and diatomite (CD 8006) adsorbent at different pH (Shaking time = 120 minutes, 0.5 g ,50 ml)

Experiment No.		Adsorbent		pH As(III)		pH As(V)		Co(mg/l)		Ce(mg/l)		%removal		Ave.%removal		SD.%removal	
		As(III)	As(V)	Before	After	Before	After	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
1	1	CD 4006	CD 8006	4.06	4.93	4.06	4.90	9.76	10.00	1.48	1.06	84.84	89.40	84.73	89.70	0.14	0.42
	2			4.07	4.80	4.06	4.90	9.76	10.00	1.50	1.00	84.63	90.00				
2	1	CD 4006	CD 8006	5.03	5.09	5.00	5.00	9.76	10.00	1.46	0.98	85.04	90.20	85.14	90.00	0.14	0.28
	2			5.05	5.07	5.00	4.95	9.76	10.00	1.44	1.02	85.25	89.80				
3	1	CD 4006	CD 8006	6.02	5.21	6.03	5.15	9.76	10.00	1.61	1.03	83.50	89.70	83.25	89.65	0.36	0.07
	2			6.05	5.19	6.05	5.11	9.76	10.00	1.66	1.04	82.99	89.60				
4	1	CD 4006	CD 8006	6.97	5.26	7.01	5.35	9.76	10.00	1.66	1.03	82.99	89.70	83.20	89.65	0.29	0.07
	2			7.00	5.22	7.01	5.25	9.76	10.00	1.62	1.04	83.40	89.60				
5	1	CD 4006	CD 8006	7.98	5.24	8.02	5.42	9.76	10.00	1.67	1.05	82.89	89.50	83.09	89.45	0.29	0.07
	2			8.02	5.32	8.02	5.46	9.76	10.00	1.63	1.06	83.30	89.40				
6	1	CD 4006	CD 8006	9.00	5.40	9.03	5.44	9.76	10.00	1.86	1.06	80.94	89.40	81.05	89.30	0.14	0.14
	2			9.09	5.52	9.03	5.44	9.76	10.00	1.84	1.08	81.15	89.20				

Table C.4 Data of percentage As(III) andAs(V) removal by diatomite(CD4006) adsorbent and diatomite (CD 8006) adsorbent at different contact time (pH = 5, 0.5 g adsorbent,50 ml)

Experiment No.		Time (min) As(III)	As(V)	pH As(III) Before	After	pH As(V) Before	After	Co(mg/l) As(III)	As(V)	Ce(mg/l) As(III)	As(V)	%removal As(III)	As(V)	Ave.%removal As(III)	As(V)	SD.%removal As(III)	As(V)
1	1	30	30	5.00	4.95	4.95	4.90	9.76	10.00	1.50	1.01	84.63	89.90	84.53	89.95	0.14	0.07
	2			5.06	4.87	5.01	4.90	9.76	10.00	1.52	1.00	84.43	90.00				
2	1	60	60	5.00	4.86	5.05	4.90	9.76	10.00	1.48	0.98	84.84	90.20	84.94	90.20	0.14	0.00
	2			5.00	4.76	5.07	5.07	9.76	10.00	1.46	0.98	85.04	90.20				
3	1	90	90	5.00	4.83	5.05	4.91	9.76	10.00	1.44	0.96	85.25	90.40	85.14	90.50	0.14	0.14
	2			5.06	4.85	5.00	4.91	9.76	10.00	1.46	0.94	85.04	90.60				
4	1	120	120	5.06	4.95	5.01	5.01	9.76	10.00	1.44	0.94	85.25	90.60	85.04	90.50	0.29	0.14
	2			5.06	4.94	5.01	5.00	9.76	10.00	1.48	0.96	84.84	90.40				
5	1	150	150	5.08	4.83	5.05	5.00	9.76	10.00	1.36	0.96	86.07	90.40	85.96	90.40	0.14	0.00
	2			5.00	4.85	5.05	5.00	9.76	10.00	1.38	0.96	85.86	90.40				
6	1	180	180	5.05	4.83	5.07	5.00	9.76	10.00	1.34	0.96	86.27	90.40	86.17	90.60	0.14	0.28
	2			5.04	4.85	5.07	5.00	9.76	10.00	1.36	0.92	86.07	90.80				
7	1	240	240	5.04	4.83	5.01	5.00	9.76	10.00	1.34	0.90	86.27	91.00	86.37	91.20	0.14	0.28
	2			5.04	4.85	5.01	5.00	9.76	10.00	1.32	0.86	86.48	91.40				
8	1	300	300	5.04	4.86	5.01	5.00	9.76	10.00	1.30	0.86	86.68	91.40	86.58	91.30	0.14	0.14
	2			5.04	4.85	5.01	5.00	9.76	10.00	1.32	0.88	86.48	91.20				
9	1	360	360	5.04	4.83	5.01	5.00	9.76	10.00	1.32	0.86	86.48	91.40	86.58	91.20	0.14	0.28
	2			5.04	4.85	5.01	5.00	9.76	10.00	1.30	0.90	86.68	91.00				
10	1	420	420	5.04	4.83	5.01	5.00	9.76	10.00	1.32	0.92	86.48	90.80	86.58	91.10	0.14	0.42
	2			5.04	4.85	5.01	5.00	9.76	10.00	1.30	0.86	86.68	91.40				

Table C.5 Data of percentage As(III) andAs(V) removal by diatomite(CD46) adsorbent and diatomite (CD 86) adsorbent at different amount of diatomite adsorbents
(pH = 5, shaking 300 minutes ,50 ml)

Experiment	No.	Weight Adsorbent (g)		pH As(III)		pH As(V)		Co(mg/l)		Ce(mg/l)		%removal		Ave.%removal		SD.%removal	
		As(III)	As(V)	Before	After	Before	After	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
1	1	0.10	0.10	5.05	5.01	5.04	5.01	9.76	10.00	3.02	2.98	69.06	70.20	69.26	70.30	0.29	0.14
	2			5.05	5.01	5.04	5.05	9.76	10.00	2.98	2.96	69.47	70.40				
2	1	0.50	0.50	5.05	5.02	5.04	5.02	9.76	10.00	1.32	0.83	86.48	91.70	86.37	91.80	0.14	0.14
	2			5.05	5.02	5.04	5.02	9.76	10.00	1.34	0.81	86.27	91.90				
3	1	1.00	1.00	5.05	5.02	5.04	5.02	9.76	10.00	0.66	0.50	93.24	95.00	93.44	95.10	0.29	0.14
	2			5.05	5.02	5.04	5.02	9.76	10.00	0.62	0.48	93.65	95.20				
4	1	2.00	2.00	5.05	5.02	5.04	5.02	9.76	10.00	0.34	0.18	96.52	98.20	96.62	98.10	0.14	0.14
	2			5.05	5.02	5.04	5.02	9.76	10.00	0.32	0.20	96.72	98.00				
5	1	3.00	3.00	5.05	5.00	5.04	5.02	9.76	10.00	0.14	0.10	98.57	99.00	98.72	99.05	0.22	0.07
	2			5.05	5.00	5.04	5.02	9.76	10.00	0.11	0.09	98.87	99.10				
6	1	4.00	4.00	5.05	5.00	5.04	5.02	9.76	10.00	0.05	0.03	99.49	99.70	99.49	99.60	0.00	0.14
	2			5.05	5.00	5.04	5.02	9.76	10.00	0.05	0.05	99.49	99.50				

Table C 6   Effects of (PO_4^{3-})on As (V) and As (III) removal

$[PO_4^{3-}]$ (mg/l)	No.	Weight Adsorbent (g)		pH As(III)		pH As(V)		Co(mg/l)		Ce(mg/l)		%removal		Ave.%removal		SD.%removal	
		As(III)	As(V)	Before	After	Before	After	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
0	1	3.00	3.00	5.09	4.95	5.00	5.02	9.76	10.00	0.13	0.10	98.67	99.00	98.77	99.05	0.14	0.07
	2			5.10	4.99	5.05	5.00	9.76	10.00	0.11	0.09	98.87	99.10				
10	1	3.00	3.00	5.00	4.89	5.07	5.01	9.76	10.00	0.37	0.17	96.21	98.30	96.57	98.40	0.51	0.14
	2			5.00	4.92	5.05	4.97	9.76	10.00	0.30	0.15	96.93	98.50				
100	1	3.00	3.00	5.00	4.92	5.04	4.95	9.76	10.00	0.49	0.19	94.98	98.10	94.98	98.20	0.00	0.14
	2			5.00	4.85	5.03	4.94	9.76	10.00	0.49	0.17	94.98	98.30				
500	1	3.00	3.00	5.01	5.04	5.00	4.99	9.76	10.00	0.51	0.19	94.77	98.10	94.72	98.05	0.07	0.07
	2			5.05	5.05	5.03	5.02	9.76	10.00	0.52	0.20	94.67	98.00				
1000	1	3.00	3.00	5.04	5.14	5.07	5.14	9.76	10.00	0.57	0.26	94.16	97.40	94.42	97.30	0.36	0.14
	2			5.00	5.15	5.00	5.12	9.76	10.00	0.52	0.28	94.67	97.20				

Table C 7 Effects of (NO_3^{2-})on As (V) and As (III) removal

[NO_3^{2-}] (mg/l)	No.	Weight Adsorbent (g) As(III)	As(V)	pH As(III) Before	After	pH As(V) Before	After	Co(mg/l) As(III)	As(V)	Ce(mg/l) As(III)	As(V)	%removal As(III)	As(V)	Ave.%removal As(III)	As(V)	SD.%removal As(III)	As(V)
0	1	3.00	3.00	5.09	4.95	5.00	5.02	9.76	10.00	0.13	0.10	98.67	99.00	98.77	99.05	0.14	0.07
	2			5.10	4.99	5.05	5.00	9.76	10.00	0.11	0.09	98.87	99.10				
10	1	3.00	3.00	5.05	4.85	5.00	5.01	9.76	10.00	0.23	0.15	97.64	98.50	97.69	98.40	0.07	0.14
	2			5.10	4.74	5.02	5.04	9.76	10.00	0.22	0.17	97.75	98.30				
100	1	3.00	3.00	4.99	4.58	5.00	5.06	9.76	10.00	0.24	0.17	97.54	98.30	97.64	98.30	0.14	0.00
	2			4.97	4.53	5.03	4.99	9.76	10.00	0.22	0.17	97.75	98.30				
500	1	3.00	3.00	4.99	4.49	5.01	4.85	9.76	10.00	0.23	0.17	97.64	98.30	97.69	98.35	0.07	0.07
	2			4.97	4.44	5.07	4.80	9.76	10.00	0.22	0.16	97.75	98.40				
1000	1	3.00	3.00	5.02	4.27	5.00	4.77	9.76	10.00	0.22	0.17	97.75	98.30	97.80	98.35	0.07	0.07
	2			5.00	4.34	5.09	4.72	9.76	10.00	0.21	0.16	97.85	98.40				

Table C 8 Effects of (CO_3^{2-})on As (V) and As (III) removal

[CO_3^{2-}] (mg/l)	No.	Weight Adsorbent (g) As(III)	As(V)	pH As(III) Before	After	pH As(V) Before	After	Co(mg/l) As(III)	As(V)	Ce(mg/l) As(III)	As(V)	%removal As(III)	As(V)	Ave.%removal As(III)	As(V)	SD.%removal As(III)	As(V)
0	1	3.00	3.00	5.09	4.95	5.00	5.02	9.76	10.00	0.13	0.10	98.67	99.00	98.77	99.05	0.14	0.07
	2			5.10	4.99	5.05	5.00	9.76	10.00	0.11	0.09	98.87	99.10				
10	1	3.00	3.00	4.96	4.96	5.04	5.00	9.76	10.00	0.28	0.14	97.13	98.60	97.28	98.80	0.22	0.28
	2			5.06	4.99	5.05	5.00	9.76	10.00	0.25	0.10	97.44	99.00				
100	1	3.00	3.00	5.05	4.80	5.07	4.97	9.76	10.00	0.26	0.13	97.34	98.70	97.34	98.60	0.00	0.14
	2			5.06	4.79	5.08	4.89	9.76	10.00	0.26	0.15	97.34	98.50				
500	1	3.00	3.00	5.04	4.65	5.04	4.78	9.76	10.00	0.25	0.17	97.44	98.30	97.44	98.35	0.00	0.07
	2			5.02	4.69	5.05	4.74	9.76	10.00	0.25	0.16	97.44	98.40				
1000	1	3.00	3.00	5.01	4.67	5.01	4.63	9.76	10.00	0.27	0.15	97.23	98.50	97.34	98.55	0.14	0.07
	2			5.03	4.63	5.02	4.66	9.76	10.00	0.25	0.14	97.44	98.60				

Table C 9 Effects of (Cl⁻)on As (V) and As (III) removal

[Cl] (mg/l)	No.	Weight Adsorbent (g) As(III)	As(V)	pH As(III) Before	After	pH As(V) Before	After	Co(mg/l) As(III)	As(V)	Ce(mg/l) As(III)	As(V)	%removal As(III)	As(V)	Ave.%removal As(III)	As(V)	SD.%removal As(III)	As(V)
0	1	3.00	3.00	5.09	4.95	5.00	5.02	9.76	10.00	0.13	0.10	98.67	99.00	98.77	99.05	0.14	0.07
	2			5.10	4.99	5.05	5.00	9.76	10.00	0.11	0.09	98.87	99.10				
10	1	3.00	3.00	5.00	4.57	5.02	5.13	9.76	10.00	0.26	0.11	97.34	98.90	97.39	99.00	0.07	0.14
	2			5.04	4.57	5.09	4.97	9.76	10.00	0.25	0.09	97.44	99.10				
100	1	3.00	3.00	5.05	4.48	5.06	4.93	9.76	10.00	0.27	0.11	97.23	98.90	97.28	99.00	0.07	0.14
	2			5.08	4.43	5.05	4.92	9.76	10.00	0.26	0.09	97.34	99.10				
500	1	3.00	3.00	5.08	4.25	5.01	4.70	9.76	10.00	0.26	0.15	97.34	98.50	97.44	98.65	0.14	0.21
	2			5.10	4.17	5.00	4.72	9.76	10.00	0.24	0.12	97.54	98.80				
1000	1	3.00	3.00	5.10	4.02	5.00	4.68	9.76	10.00	0.26	0.14	97.34	98.60	97.39	98.65	0.07	0.07
	2			5.10	3.94	5.00	4.69	9.76	10.00	0.25	0.13	97.44	98.70				

Table C10 Effect of mix ion on As(III) and As(V) removal

Mix ion (mg/l)	No.	Weight Adsorbent (g) As(III)	As(V)	pH As(III) Before	After	pH As(V) Before	After	Co(mg/l) As(III)	As(V)	Ce(mg/l) As(III)	As(V)	%removal As(III)	As(V)	Ave.%removal As(III)	As(V)	SD.%removal As(III)	As(V)
0	1	3.00	3.00	5.09	4.95	5.00	5.02	9.76	10.00	0.13	0.10	98.67	99.00	98.77	99.05	0.14	0.07
	2			5.10	4.99	5.05	5.00	9.76	10.00	0.11	0.09	98.87	99.10				
100	1	3.00	3.00	5.05	4.75	5.08	4.98	9.76	10.00	0.26	0.10	97.34	99.00	97.28	99.05	0.07	0.07
	2			4.95	4.73	4.95	4.90	9.76	10.00	0.27	0.09	97.23	99.10				

Table C-11 The data using for Freudlich isotherm

M (g)	Co (mg/L)		Ce (mg/L)		C (mg)		X (mg)		X/M (mg/g)		log (C)		log (X/M)	
	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
0.000	9.760	10.000	9.760	10.000	0.488	0.500	-	-	-	-	-0.312	-	0.000	-
0.100	9.760	10.000	6.530	2.970	0.327	0.149	0.340	0.352	3.380	3.515	-0.486	-0.828	0.529	0.546
0.500	9.760	10.000	1.310	0.820	0.066	0.041	0.447	0.459	0.845	0.918	-1.184	-1.387	-0.073	-0.037
1.000	9.760	10.000	0.630	0.490	0.032	0.025	0.464	0.476	0.457	0.476	-1.502	-1.611	-0.341	-0.323
2.000	9.760	10.000	0.330	0.190	0.017	0.010	0.479	0.491	0.236	0.245	-1.783	-2.022	-0.628	-0.610
3.000	9.760	10.000	0.060	0.100	0.003	0.005	0.483	0.495	0.161	0.165	-2.523	-2.301	-0.795	-0.783
4.000	9.760	10.000	0.050	0.050	0.003	0.003	0.486	0.498	0.121	0.124	-2.602	-2.602	-0.916	-0.905

Table C-12 The data using for Langmuir isotherm

M (g)	Co (mg/L)		Ce (mg/L)		C (mg)		X (mg)		q (mg/g)		1/Ce (L/mg)		1 /(q) (g/mg)	
	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
0.000	9.760	10.000	9.760	10.000	0.488	0.500	-	-	-	-	-	-	-	-
0.100	9.760	10.000	3.000	2.970	0.150	0.149	0.338	0.352	3.380	0.036	0.333	0.337	0.296	0.284
0.500	9.760	10.000	1.310	0.820	0.066	0.041	0.4215	0.442	0.843	0.883	0.763	1.220	1.186	1.133
1.000	9.760	10.000	0.630	0.490	0.032	0.025	0.456	0.476	0.456	0.476	1.587	2.041	2.193	2.103
2.000	9.760	10.000	0.330	0.190	0.017	0.010	0.4715	0.486	0.236	0.243	3.030	5.263	4.242	4.115
3.000	9.760	10.000	0.130	0.100	0.007	0.005	0.482	0.488	0.161	0.163	7.692	10.000	6.224	6.154
4.000	9.760	10.000	0.050	0.050	0.003	0.003	0.4855	0.493	0.121	0.123	20.000	20.000	8.239	8.122

Table C13 Data of the percentage removal of arsenic from arsenic contaminated surface water by using CD4006 and CD8006 adsorbents

No.	Weight Adsorbent (g)		pH of CD4006		pH of CD8006		Co(mg/l)	Ce(mg/l)		% As removal		Ave.% As removal		SD.%As removal	
	CD4006	CD8006	Before	After	Before	After		CD4006	CD8006	CD4006	CD8006	CD4006	CD8006	CD4006	CD8006
1	0.10	0.10	5.06	4.74	5.06	4.74	1.80	0.05	0.05	97.22	97.22	97.42	97.42	0.28	0.28
2	0.10	0.10	5.06	4.72	5.06	4.75	2.10	0.05	0.05	97.62	97.62				
1	0.50	0.50	5.06	4.73	5.06	4.78	1.80	0.05	0.05	97.22	97.22	97.42	97.42	0.28	0.28
2	0.50	0.50	5.06	4.73	5.06	4.80	2.10	0.05	0.05	97.62	97.62				
1	1.00	1.00	5.06	4.65	5.06	4.66	1.80	0.05	0.05	97.22	97.22	97.42	97.42	0.28	0.28
2	1.00	1.00	5.06	4.64	5.06	4.66	2.10	0.05	0.05	97.62	97.62				
1	2.00	2.00	5.06	4.63	5.06	4.76	1.80	0.05	0.05	97.22	97.22	97.42	97.42	0.28	0.28
2	2.00	2.00	5.06	4.64	5.06	4.75	2.10	0.05	0.05	97.62	97.62				

The calculation examples for determined the q_{max} based on the Freundlich equation

1. Figure 4.12 the Fruendlich Isotherm of As (III) removal using CD4006 adsorbent

$$y = 1.1248x + 0.1329$$

$$\text{Slope} = 1.1248$$

$$y - \text{Intercept} = 0.1329$$

The Freundlich equation

$$q = K_f C^{1/n}$$

Slope $= 1/n = 1.1248$

$y - \text{Intercept} = K_f = 0.1329$

C = 10 mg/l

$$q = 0.1329 \times 10^{1.1248}$$

$$q = 1.77 \text{ mg/g}$$

2. Figure 4.14 the Fruendlich Isotherm of As (V) removal using CD4006 adsorbent

$$y = 0.7889x + 0.0901$$

$$\text{Slope} = 0.7889$$

$$y - \text{Intercept} = 0.0901$$

The Freundlich equation

$$q = K_f C^{1/n}$$

Slope $= 1/n = 0.7889$

$y - \text{Intercept} = K_f = 0.0901$

C = 10 mg/l

$$q = 0.0901 \times 10^{0.7889}$$

$$q = 0.55 \text{ mg/g}$$

BIOGRAPHY

Miss Mathuros Sangpairoj was born on October, 1978 in Bangkok, Thailand. She received her Bachelor Degree in Environmental Science and Technology from Faculty of Environment and Resource Studies Mahidol University in 2001. She worked as environmental scientist at Environmental Research and Training Center (ERTC) in June, 2001. Since then, she had been studying for a Master Degree of Science Program in Environmental Science (Interdisciplinary Program) at Chulalongkorn University in June, 2003.