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THE REMOVAL OF ARSENIC FROM DRINKING WATER
BY CARBON ADSORPTION

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# THE REMOVAL OF ARSENIC FROM DRINKING WATER BY CARBON ADSORPTION

By

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# ABSTRACT

## THE REMOVAL OF ARSENIC FROM DRINKING WATER BY CARBON ADSORPTION

By

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It is estimated that millions of people who are drinking arsenic contaminated groundwater are suffering from arsenic related diseases such as skin, bladder and kidney cancer in Bangladesh. The system to remove arsenic must be economically feasible for the members of affected communities. In a recent report, Ansari et al have concluded that carbon adsorption, which is a comparatively cheap and easy to operate method, is a potentially feasible method for the removal of arsenic. The present study focused on activated carbon as an adsorbent and four different types of activated carbon, which are CPG-LF, F400, OLC and DSR-C, were tested. Both batch and column experiments were conducted to observe the adsorptive kinetics and capacity of each activated carbon. Arsenic is present in natural water as As(V) or As(III), and all four activated carbons removed As(V) effectively. As(III), which is more toxic than As(V), was also effectively removed by CPG-LF in the batch tests. By evaluating the adsorptive kinetics and capacity of each activated carbon, it was concluded that CPG-LF is the best carbon adsorbent of the four activated carbons for arsenic removal.

To my parents, fiancée, and people in Bangladesh

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# INTRODUCTION

Arsenic, which is a naturally occurring element, contaminates groundwater in many countries such as Argentina, Australia, Bangladesh, Chile, Hungary, India, Mexico, Peru, Taiwan, Thailand, and the United States (WHO, 2001). Among these countries, the severest problem occurs in Bangladesh where up to 90% of the rural inhabitants depend on groundwater for drinking. According to a British Geological Survey (BGS), 28 to 35 million people are exposed to arsenic concentrations above 50 ppb and the number of people exposed to more than 10 ppb is 46 to 57 million (BGS, 2000). It is estimated that millions of people in Bangladesh are suffering from arsenic related disease such as skin, lung, bladder, and kidney cancer, and among them about twenty thousand people die each year, according to the UN Development Program.

There are some effective technologies to treat arsenic contamination, such as chemical precipitation, ion exchange and membrane methods. However, these treatments are expensive and are not easy to operate, so the introduction of these techniques to developing nations, such as Bangladesh, is questionable. In a recent report, Ansari et al has concluded that carbon adsorption, which is comparatively cheap and easy to operate, is a potentially feasible method for the removal of arsenic after testing several different kinds of adsorbents, such as zeolite, chabazite, clinoptiolite and activated carbon (Ansari, 2000).

This study focused on only activated carbon as an adsorbent. Four different types of activated carbon were tested. The primary objective of this study was to evaluate the best carbon adsorbent for arsenic removal, observing the differences in the adsorption kinetics and capacity.

The ultimate goal of this study is to propose a treatment for the groundwater in Bangladesh. Arsenic is found mainly in two forms: trivalent arsenite [As(III)] and pentavalent arsenate [As(V)]. As(III), which is more toxic than As(V), becomes predominant species in groundwater. Though most wells affected by arsenic in Bangladesh are shallow wells (12-70m depth), arsenic can be in the reduced form As(III) since the oxidation rate of As(III) is slow (Smedley, 2001). Indeed, arsenic speciation studies revealed that the proportion of arsenite in well water in Bangladesh is between 50% to 60% of total arsenic (BGS and DHPE, 2001). Therefore, the effect of arsenic oxidation state in the adsorption process is significant in addressing this problem. A secondary objective of this study is to observe how well activated carbon adsorbs arsenic in the reduced form As(III).

The removal system must be economically feasible for members of affected communities. Several treatment systems are available in

Bangladesh such as using the Safi filter and Kolshi filter (Jakariya, 2000). Comparison among available techniques with activated carbon must be done in terms of removal efficiency and cost. Activated carbon is considered to be cost competitive point of use method. This study will provide people in Bangladesh with an economical and easy-to-use treatment process.

# 1. Background

## 1.1. Arsenic Regulation

World:

An international standard of 0.20 mg/L (200 ppb) was established as the allowable level for arsenic in 1958. In 1963 the standard was reevaluated and reduced to 0.05 mg/L (50 ppb). In 1984 this was maintained as World Health organization's (WHO) guideline value and many countries have kept this as the national standard. In 1993, 0.01 mg/L (10 ppb) was established as WHO's provisional guideline value for arsenic in drinking water based on analytical capability (WHO, 2001). The Japanese standard for drinking water is 10 μg/L and the maximum permissible concentration for As in Canada is 25 μg/L. However, most of the drinking water standards in developing nations are still in the range of 0.04 to 0.05 mg/L. This is partly because there is no adequate testing facilities for lower concentrations in those countries.

United States:

The current arsenic standard of 50 ppb was set by U.S. Environmental Protection Agency (USEPA) in 1975 based on a Public Health Service standard set in 1942. Under the 1996 SDWA (The Safe Drinking Water Act) amendment, the USEPA was required to propose a new standard for arsenic in drinking water. In January 2001, the USEPA proposed lowering the amount of arsenic allowed in drinking water from 50 ppb to 10 ppb based on the evidence of cancer risk from high arsenic doses in Taiwan and Chile (Smendley, 2001). A few months later, the new administrator of the EPA announced a delay in the implementation of the new standard on the basis that the scientific indicators are unclear as to whether the standard needs to go as low as 10 ppb. Currently it is under consideration, and a revised standard between 3 ppb and 20 ppb will be announced by February 2002 (Franz, 2001).

Bangladesh:

The national standard for drinking water in Bangladesh is 0.05 mg/L (50 ppb) that was established by following the WHO guideline (WHO, 2001).

## 1.2. Source

Arsenic is widely distributed throughout the earth's crust and commonly found in rocks and soils with a high sulfur content. Arsenic is introduced into water through the dissolution of minerals and ores, and by agricultural application such as pesticides, herbicides and insecticides.

Mining and industrial effluent also contribute arsenic to water in some areas.

In Bangladesh, dissolution of natural minerals causes arsenic to be released into groundwater. There appears to be three distinct dissolution processes that can release arsenic from mineral sources into groundwater. The first is an increase of pH to levels above pH 8.5. This increase of pH leads to desorption of adsorbed arsenic from mineral sources. The second process results from the development of reducing conditions. The reducing condition converts arsenic species from arsenate to arsenite and it results in the release of arsenic from minerals. The third potential process involves the oxidation of sulfide minerals. Arsenic is released from sulfide minerals as they are oxidized by natural weathering processes. Released arsenic can leach into the groundwater and be transported to water supply wells.

Arsenate is well adsorbed onto the surface of minerals. The adsorption of arsenate by iron oxides plays an important role preventing widespread arsenic toxicity problems in nature. Arsenite is a neutral molecule at near neutral pH range and is therefore less adsorbed on most mineral surfaces than arsenate. Thus, arsenite is generally more mobile than arsenate and may be more likely contaminate water supplies (Smendley, 2001).

## 1.3. Speciation

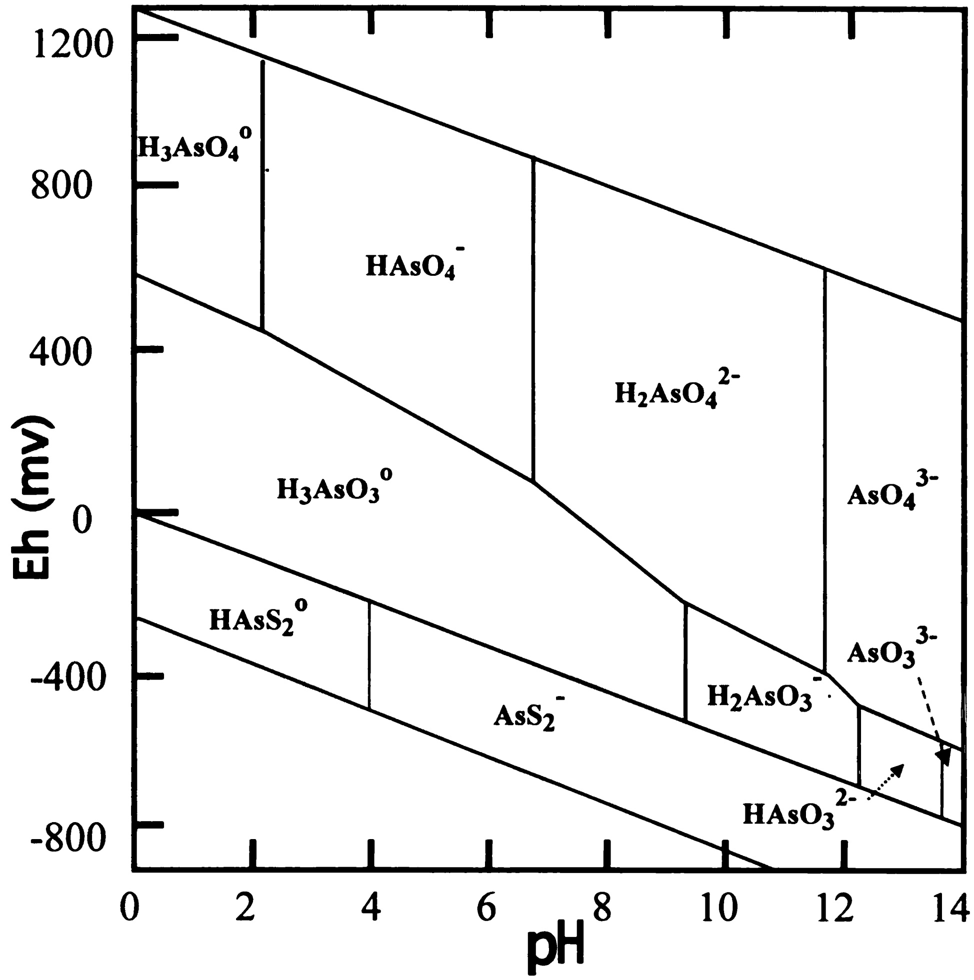

Figure1: Eh-pH diagram for Arsenic Species at 25 °C (Korte, 1991) (Smedley, 2000)

Figure1 is a plot of the redox potential (Eh) versus pH for the arsenic species. The Eh-pH diagram, which indicates the predominant species in solution, is the important factor for arsenic speciation. The domain of each species is defined by the solid lines. At the boundaries of two domains, two species have equal activities (Cullen and Reimer, 1989). Arsenic occurs in the environment in several oxidation states (-3, 0, +3, +5). In natural water arsenic is mostly found in inorganic form as trivalent arsenite [As(III)] or pentavalent arsenate [As(V)]. Arsenate has four species: $H_3AsO_4$, $H_2AsO_4^-$, $HAsO_4^{2-}$ and $AsO_4^{3-}$ with pKa values of 2.2, 6.9 and 11.5. Arsenite also has four species: $H_3AsO_3$, $H_2AsO^{3-}$, $HAsO_3^{2-}$ and $AsO_3^{3-}$ with pKa values of 9.2, 12.1 and 13.4 (Cullen and Reimer, 1989). It is apparent that in surface water under oxidizing condition, the As(V) species is predominant. On the other hand, in anoxic water under reducing condition, the As(III) species becomes stable. At near neutral pH, the predominant species are $H_2AsO_4^-$ and $HAsO_4^{2-}$ for arsenate, and uncharged $H_3AsO_3$ for arsenite.

## 1.4. Toxicity

The toxicity of arsenic is dependent on its chemical form. Arsenite is considered to be more toxic than arsenate according to several researches. Inorganic arsenic is combined with sulfhydryl groups in proteins and is accumulated in human bodies. Since arsenite has higher affinity for proteins than arsenate, arsenite is more toxic. Arsenate can be reduced to arsenite by the activity of glutathione and results in the same toxicity. However, since not all of the arsenate can be converted to arsenite, the toxicity of arsenate is less than arsenite.

The toxicity of inorganic arsenic can be reduced by methylation. In the methylation process, inorganic arsenic is converted to methyl arsenic which is less toxic and is primarily excreted in urine.

Human sensitivity to the toxic effects of inorganic arsenic exposure is likely to vary based on genetic differences, diet, health conditions, sex and other possible factors. These factors are important in the risk assessment to arsenic exposure. For example, people with less ability to methylate arsenic might accumulate more arsenic in their tissues and may be more at risk of developing toxic effects. One study indicates that children and people in poor nutritional conditions might have a decreased ability to methylate arsenic (NAS, 1999).

## 1.5. Health Effect

In 1980, the International Agency for Research on Cancer (IARC) determined that inorganic arsenic compounds are skin and lung carcinogens in humans. Over the years arsenic is accumulated in humans bodies and the physical symptoms emerge after a decade or more of drinking contaminated water. The evidence from human studies in Taiwan, Chile and Argentina indicates that long term exposure to arsenic may cause skin, lung, bladder, and kidney cancer. Levels of arsenic in water at 50 ppb may result in a combined cancer risk of one out of one hundred. To lower the cancer risk to 1/10,000, which is considered to be an acceptable risk, the concentration of arsenic in drinking water needs to be reduced to 2 μg/L (2 ppb) according to the National Academy of Sciences (NAS, 1999).

## 1.6. Removal Technology

### 1.6.1. Coagulation/Precipitation followed by Filtration

Arsenic coagulation with metal salts has been demonstrated since 1934. The most commonly used metal salts are aluminum salts such as alum, and ferric salts such as ferric chloride. Laboratory scale tests report that both alum and ferric chloride can remove arsenic efficiently under optimal conditions (Cheng et al., 1994). The optimal conditions vary among coagulants. Coagulation with ferric chloride works effectively at pH below 8 (Edwards, 1994). Alum works effectively in a narrower pH range from 6 to 7 (Hering et al., 1997). In general, high dosage of coagulant achieves high removal efficiency. Typical doses of ferric chloride and alum for arsenic removal are 5 to 30 mg/L and 10 to 50 mg/L, respectively.

The mechanisms of coagulation are described as follows. Alum and ferric chloride dissolve into solution and form amorphous hydrous aluminum oxide (HAO) and ferric oxide (HFO), respectively. These metal hydroxides form flocs and bind to other flocs. Flocs grow until they get heavy enough to settle down. Soluble arsenic species are physically involved in the process of the formation of flocs and are co-precipitated. Soluble arsenic species are also adsorbed on the external surface of the insoluble metal hydroxide and are precipitated.

Similar removal efficiencies were achieved with either ferric chloride or alum for As(V). However, As(III) is less efficiently removed than As(V) by coagulant especially using alum, so pre-oxidation is necessary for better removal. The reason ferric chloride removes As(III) more efficiently than alum is that ferric chloride oxidize the arsenite to arsenate and the formed arsenate is removed by coagulation (Edwards, 1994).

Lime softening, which is a conventional treatment process, is also effective to remove the arsenic species. This process works effectively in the pH range of 10.5 to 12 for the removal of arsenate. The main mechanism was found to be the sorption of arsenic onto magnesium hydroxide solids that is formed during softening. Arsenite is not removed effectively by lime softening process (Johnston et al., 2001).

### 1.6.2. Ion exchange

Ion exchange is commonly used in water softening, but some ion exchange resins work effectively for removing arsenic. Strong base anion exchange resins, which are used to remove anion species, are usually used to remove arsenic. This resin only works for removing arsenate that is negatively charged above pH 2.2. Negatively charged arsenate is strongly attracted to sorption sites on the surface of the resin and effectively removed from the solution. However, arsenite is not removed by the resin because of its uncharged form below pH 9.2 in solution. Therefore, if water contains arsenite, a pre-oxidation process is necessary to achieve better removal. Ion exchange resins are usually used in a packed bed or column. A bed can treat several hundred to a thousand bed volumes before arsenic breakthrough occurs. The run length of a column is dependent on the competing anion species in solution. The selectivity of sulfate is especially high for anion exchange resins, so the run length becomes shorter with high concentration of sulfate. Ion exchange resins work effectively with sulfate concentration of under 120 mg/L according to EPA (USEPA, 2000). Ion exchange capacity is usually measured in a unit of meq/mL. Typical theoretical capacity of strong base anion exchange resin ranges from 1.0 to 1.4 meq/mL, which is converted to 315 mg As/g (Clifford, 1999). However, an actual study using laboratory reagents found that the operational capacity of anion exchange resin to be about 64 mg As/g (Baes et al., 1997). When the resin is saturated, ion exchange resin is regenerated with concentrated salt solution (Johnston et al, 2001) (Wang et al, 2000).

### 1.6.3. Activated Almina

Activated alumina is a granular form of aluminum oxide ($Al_2O_3$) with a high internal surface area in the range of 200-300 $m^2/g$. Activated alumina is usually used in packed beds. The kinetics of arsenic adsorption onto activated alumina surface are slower than those onto ion exchange resins, but usually it has longer run times than ion exchange. Typically, several thousands of beds volume can be treated before arsenic is saturated. One study showed that under optimal condition, activated alumina treated arsenate with an influent concentration of 100 μg/L (100 ppb) for 10,000 to 20,000 bed volumes before gradual breakthrough was observed (Frank and Clifford, 1986). These investigators also reported that the capacity of activated alumina for arsenic adsorption is 4 mg of As/g of activated alumina under optimal condition. Activated almina works effectively in the pH range of 5.5 to 6.0, and above pH 7.0 removal efficiency drops sharply (Clifford, 1999). Arsenate is more effectively removed by activated alumina than arsenite. Therefore, for better results, raw water containing arsenite should be oxidized before treatment. Saturated activated almina can be regenerated by flushing with strong base such as sodium hydroxide followed by strong acid, which re-establishes a positive charge on the surface (Johnston et al, 2001) (Wang et al, 2000).

### 1.6.4. Membrane Process (RO/Nanofiltration)

The membrane process allows water and small molecules to pass through but rejects larger molecules and particles. The removal efficiency using the membrane process is independent of pH but depends on the molecular size of substance being removed. High pressure membranes such as reverse osmosis (RO) and nanofiltration have appropriate pore size for removal of dissolved arsenic. Recent studies showed that both reverse osmosis and nanofiltration are equally effective for both arsenic in reduced form and oxidized form at pressures ranging from 40 to 400 psi. Therefore, membrane processes seem most suitable for arsenic removal from groundwater in which most of the arsenic is present in reduced form. A study has shown that the arsenic removal using a membrane process is independent of pH, so there is no need to adjust pH (Waypa et al, 1997).

The fouling of membranes is a primary disadvantage of this process. Constituents such as organic matter, iron and manganese can foul membranes. Therefore, the membrane processes usually require pretreatment of raw water in order to prevent fouling. Membrane systems are generally more expensive than other arsenic removal options (Johnston et al, 2001).

### 1.6.5. Oxidation

Oxidation itself does not remove arsenic from drinking water, but oxidation is often useful to optimize other treatment processes. Most arsenic removal technologies are not so effective in removing arsenite because arsenite is uncharged below pH 9.2. Therefore many treatment systems include the oxidation step in removal processes.

Oxidation of arsenite by dissolved oxygen is a particularly slow reaction.

Cherry and others reported that even when distilled water spiked with arsenite (pH 7) is saturated with oxygen, arsenite stayed uncharged for days (Cherry et al., 1979). The oxidation rate of arsenic is dependent on the concentration of dissolved oxygen in solution. Therefore when water is saturated with air instead of pure oxygen, the oxidation rate becomes slower. Kim and Nriagu showed that the half-life of arsenite in water saturated with pure oxygen and air is 2-5 days and 4-9 days, respectively (Kim and Nriagu, 2000). Another study reports that in natural water half-life of arsenite is 1-3 years, although the rate might be higher due to the presence of oxidants in solution (Eary and Schramke, 1990).

Adding oxidants such as chlorine, permanganate, ozone and hydrogen peroxide helps increase the rate of oxidation of arsenic. Among them, chlorine, which is widely available in developing nations, appears to be a rapid and effective oxidant for arsenic. However, it is well known that chlorine may produce toxic by-products when reacting with organic matter. If chlorine oxidation is applied to groundwater, the risk of toxic by-products will be less than that of surface water because groundwater has a less organic matter due to the natural filtering by soil. Typical doses of chlorine for oxidation of arsenite are 0.8 to 2.0 mg/L. In Europe, ozone is widely used as an oxidant in treatment process, though it has not been used in developing nations. A report showed that in water with 2 mg/L of ozone the half-life of arsenite is approximately 4 minutes (Kim and Nriagu, 2000). Potassium permanganate which is widely available in developing nations is also effective to oxidize arsenite.

There are several other options to increase the oxidation rate of arsenite without adding oxidants. A remarkable increase in the oxidation rate of arsenite was observed on exposure to sunlight (Cullen and Reimer, 1989). This is because ultraviolet radiation can catalyze the oxidation of arsenic in the presence of oxygen. It is also believed that increasing temperature or freezing solution helps accelerate the oxidation rate of arsenite (Johnston et al, 2001).

### 1.6.6. Removal Technology in Bangladesh

*Safi Filter :*

A filter called Safi filter has been developed in Bangladesh by Professor Safiullah, Jahangirnagar University. The material of the Safi filter consists of a chemical mixture of laterite soil, ferric oxide, manganese dioxide, aluminum hydroxide and mezo-porous silica. These materials remove arsenic effectively by adsorption. The Safi filter can treat approximately 40 liters per day, which is more than sufficient for the demand of a family of six. The manufacturers indicate that the materials need to be replaced after two years of continuous use. The materials cost about $4 (200 Taka) per unit, and the total cost of this filter is about $ 20 (900 Taka) per unit (BRAC, 1999). The main problem of this system is clogging that results in low flow rate of the system (Jakariya, 2000).

*Kolshi filter (Three-Pitcher Filter) :*

The Kolshi filter is made from locally available materials and has been used for many years in Bangladesh. The Kolshi filter consists of three 18-liter clay pitchers called "kolshis". A top pitcher is filled with 2 kg of coarse sand, and a second pitcher is filled with 1 kg of charcoal and 2 kg of fine sand, and a third pitcher serves as storage. Small holes are made at the bottom of the first two pitchers so that water can pass through. To adsorb more arsenic, the system has been modified by adding 3 kg of iron filing to the top pitcher, which provides an additional source of iron oxide (Rasul et al, 1999). The total cost of this system per unit is $ 5.0 (250 Taka).

Laboratory tests showed that the Kolshi filter removed arsenic effectively from well water. A wide range of arsenic concentration (from 80 to 1000 ppb) was tested using this system, and the effluent arsenic concentration of 5 to 30 ppb was measured, which is less than the arsenic standard in Bangladesh. Field tests of two hundred units confirmed that 90% of the filters produced water with no arsenic after one week of operation, and 7% produced water in which arsenic was slightly detected. The filters were still working efficiently after four months of operation. However, the field tests also showed that some slight contamination with bacteria occurred before filtration, and bacteria counts increased dramatically during filtration and storage. Near two thirds of treated water samples showed counts higher than 100 TC/100 mL. The media of filter needs to be sterilized before filter construction to avoid the risk of bacterial contamination. It is also a problem that this system produces waste material with high concentration of arsenic because no regeneration is available (Johnston et al, 2001) (Jakariya, 2000).

## 1.7. Theory of Carbon Adsorption

### 1.7.1. Mechanisms of Adsorption

Adsorption is the attachment of a substance onto the surface of adsorbent, whereas absorption is the penetration of the attached substance into solid. Since both phenomena often happen at the same time, the term sorption is sometimes used. Although both adsorption and absorption onto activated carbon occur in removal process, it is usually referred to as adsorption.

Adsorption occurs when the attraction between solute and adsorbent is greater than the attraction between solute and solvent. There are two main attraction forces between phases: van der Waals forces and electronic forces. The van der Waals forces are relatively weak interactions, whereas the electronic forces are relatively strong interactions which are sometimes irreversible.

The rate of adsorption is related to various mass transfer mechanisms. First, an adsorbate molecule is transferred from the bulk liquid to the boundary layer surrounding the adsorbent solid. Second, the adsorbate diffuses through the boundary layer to the surface of the adsorbent solid.

Third, the adsorbate diffuses through the pores into internal adsorption sites of the adsorbent solid. Usually the rate of adsorption is limited by boundary diffusion and pore diffusion (Voice, 1997) (Reynolds, 1982).

### 1.7.2. Characteristics of Activated Carbon

Activated carbon is used to remove wide a variety of contaminants in both liquid and gaseous phases. It is typically used to remove organic compounds and some inorganic compounds with the characteristics of non-polarity and low solubility.

Activated carbon is made from a number of carbonaceous materials such as coal, wood and coconut shells. The manufacturing process consists of carbonization of the materials followed by the activation using hot air or steam, which produces an extensive network of internal pores. The product that results from this process is highly porous, consisting of macropores and micropores. The size distribution is largely a function of the manufacturing process. The total internal surface area is typically in the range of 500 to 2000 $m^2/g$. The high adsorptive capacity of activated carbon is a result of high surface area of the finished product. The total surface area may provide an approximation of adsorptive capacity. However, the actual capacity for a specific compound is more closely related to the available surface area for the specific compound. A number of standardized tests using adsorbates of known molecular size has been performed. The common test adsorbate is iodine which correlates with a pore size greater than 10 Å. Activated carbon is available at low cost and can normally be regenerated (Voice, 1989) (Reynolds, 1982).

### 1.7.3. Isotherm

An isotherm is used to determine the adsorptive capacity of an adsorbent. The isotherm expresses the relation between the equilibrium concentration in solution and the amount of adsorbate adsorbed per unit mass of activated carbon. In practice, an isotherm is measured experimentally by equilibrating a known mass of adsorbent with a known initial concentration of adsorbate, and plotting the resultant concentration. However, an isotherm is quite dependent on the presence of other adsorbates and temperature. Therefore, it is always necessary to perform the isotherm using raw contaminated waste.

# 2. Methodology

## 2.1. Material

### 2.1.1. Activated Carbon

Four types of activated carbon from Calgon Carbon were tested.

CPG-LF:

CPG-LF is an acid washed granular activated carbon with a low acid soluble iron content. It is designed for the purification and decolorization of many aqueous and organic liquids. The particle size of 12×40 mesh has been selected to give a high rate of adsorption and low resistance flow. CPG-LF is made from selected grades of bituminous coal combined with suitable binders to give superior hardness and long life. It is produced under controlled conditions by high temperature steam activation, so this carbon provides high surface area. Iodine number: 950 mg of Iodine/g. Cost: $1.69 /lb = $3.72/kg.

F 400:

F 400 is a granular activated carbon designed for the removal of taste and odor compounds and dissolved organic compounds from liquid phase. This activated carbon is manufactured from select grades of bituminous coal. Activation is carefully controlled to produce high internal surface area for effective adsorption. The particle size of 8×30 mesh has been selected. F 400 is used to treat surface and ground water sources for the production of drinking water. Iodine Number: 1000 mg of Iodine/g. Cost: $1.21/lb = $2.66/kg.

OLC:

OLC is a coconut base granular activated carbon. The particle size of 12×40 mesh has been selected for this product. Iodine Number: 1100 mg of Iodine/g. Cost: $1.74/lb = $3.83/kg.

DSR-C:

DSR-C is a granular re-activated carbon designed for the removal of organic contaminants from industrial wastewater. This carbon is manufactured by the reactivation of bituminous coal. Iodine Number: 800 mg of iodine/g. Cost: $0.89/lb = $1.96/kg.

### 2.1.2. Treatment by Ferrous Sulfite

Huang and Vane reported that treated activated carbon by ferrous salt enhances the removal efficiency for As(V) because of its high affinity for arsenate (Huang and Vane, 1989). In this study four activated carbons were treated with 0.2 M of ferrous sulfate (Sigma Chemicals, St Louis). Four glass bottles with the capacity of 1 L were filled with 500 mL of DI water. The water was purged with pure nitrogen gas for 30 minutes to remove oxygen, which prevents the oxidation of ferrous sulfate to ferric sulfate. Then, 27.8 g of ferrous sulfate was weighed and added into each bottle during purging so that the chemical can be mixed well. Five grams of each of the four types of activated carbon were weighed and added into each labeled glass bottle. The four glass bottles were put on the shaker horizontally and shaken at 100 rpm for 20 hours. The pH of solution was measured before and after shaking. After 20 hours of shaking, the activated carbons were taken out of each glass bottle and put into four labeled glass vials, respectively. The activated carbons were put in an oven and dried at 120°C overnight. The weights of the final products were measured.

| | Mass of A.C. Before (g) | Mass of Ferrous Sulfate (g) | pH Before | pH After | Mass of A.C. After Dry (g) |
|---|---|---|---|---|---|
| CPG-LF | 5.0072 | 27.821 | 2.94 | 2.57 | 5.5805 |
| F400 | 5.0025 | 27.806 | 2.92 | 2.41 | 5.7018 |
| OLC | 5.0072 | 27.801 | 2.89 | 2.40 | 5.4560 |
| DSR-C | 5.0040 | 27.802 | 2.89 | 2.43 | 5.2170 |

Table 1: Weight of Adsorbents and pH Change During Treatment

Table 1 shows the difference in weights and pH before and after treatment with ferrous sulfate. This gain of weight indicates that ferrous sulfate was adsorbed onto the activated carbons.

## 2.2. Chemicals

### 2.2.1. Arsenate

Sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$, FW=312.0) was purchased from Sigma Chemicals, St. Louis. 1000 mg/L (1000 ppm) of As(V) standard solution was prepared by dissolving 0.4164 g of $Na_2HAsO_4 \cdot 7H_2O$ in a 100 ml volumetric flask.

### 2.2.2. Arsenite

Sodium arsenite ($NaAsO_2$, FW=129.9) was purchased from Sigma Chemicals, St. Louis. 1000 mg/L (1000 ppm) of As(III) standard solution was prepared by dissolving 0.17343 g of $NaAsO_2$ in a 100 ml volumetric flask.

The following reaction occurs in solution. (Korte, 1991)

$NaAsO_2 \Rightarrow Na^+ + AsO_2^-$

$H^+ + AsO_2^- \Rightarrow HAsO_2$ (below pH 9.2, reducing condition)

$H_2O + HAsO_2 \Rightarrow H_3AsO_3$ (below pH 9.2, reducing condition)

### 2.2.3. Reducing Agent

Usually ascorbic acid is used to prevent oxidation of As(III) to As(V) according to some researchers. However, adding ascorbic acid results in a low pH. Since the objective of this study is to treat the groundwater in Bangladesh, which has the pH range around neutral, the low pH is not preferable for this study. However, it is difficult to keep arsenic in a reduced form at near neutral pH range because the ORP (Oxidation-Redox Potential, unit of mV) of the solvent needs to be close to 0 mV (see Fig.1). Through experimentation, it was found that DI water has the ORP value of 150 to 190 mV. Purging with nitrogen can remove dissolved oxygen down to 0.5-0.8 mg/L. However, nitrogen bobbling does not change ORP significantly (see appendix). Therefore, to obtain a lower ORP, a reducing agent must be added into the DI water.

Three types of reducing agents were used in this study, which are sodium sulfite ($Na_2SO_3$), sodium meta-bisulfite ($Na_2S_2O_5$) and sodium thiosulfate ($Na_2S_2O_3$). A detailed chemical description is included in the appendix.

*Characteristics of Reducing Agent in Solution:*

**$Na_2SO_3$ (Sodium Sulfite):**

| | DO (mg/L) | pH | ORP (mV) |
|---|---|---|---|
| Initial Condition of DI Water | 6.3 | 7.3 | 175 |
| 3 minutes after adding | 0.25 | 9.38 | 5 |
| 1 hour after adding | 0.11 | 9.28 | 5 |
| 2 hour after adding | 0.07 | 9.16 | 10 |

Table 2. Characteristics of Sodium Sulfite in Solution

Result by Adding 0.5 g of $Na_2SO_3$ into 70 ml DI Water

As observed in Table 2, the pH goes up drastically when sodium sulfite is added into water. The ORP decreases significantly upon addition of sodium sulfite. The reaction with dissolved oxygen occurs very quickly (in a few minutes). The pH goes down slightly with time.

$Na_2S_2O_5$ (Sodium Meta-Bisulfite):

| | DO (mg/L) | pH | ORP (mV) |
|---|---|---|---|
| Initial Condition of DI Water | 6.4 | 7.2 | 175 |
| 30 minutes after adding | 0.54 | 4.23 | 105 |
| 1 day after adding (without air) | 0.23 | 4.22 | 100 |
| 2days after adding (without air) | 0.14 | 4.19 | 100 |

Table 3. Characteristics of Sodium Meta-Bisulfite in Solution

Result by Adding 0.5 g of $Na_2S_2O_5$ into 70 ml of DI Water

Table 3 shows that the pH goes down drastically when sodium meta-bisulfite is added into water. The ORP decreases remarkably after the addition of sodium meta-bisulfite. The reaction with dissolved oxygen is as fast as sodium sulfite.

$Na_2S_2O_3$ (Sodium Thio-Bisulfite):

| | DO (mg/L) | pH | ORP (mV) |
|---|---|---|---|
| Initial Condition of DI Water | 6.4 | 7.3 | 175 |
| 3 minutes after adding | 6.45 | 7.42 | 85 |
| 30 minutes after adding | 6.34 | 7.40 | 85 |
| 1 day after adding (without air) | 2.23 | 7.25 | 80 |
| 2 days after adding (without air) | 1.81 | 7.17 | 80 |

Table 4. Characteristics of Sodium Thiosulfate in Solution

Result by Adding 0.5 g of $Na_2S_2O_3$ into 70 ml of DI Water

Table 4 indicates that sodium thiosulfate does not react with dissolved oxygen as quickly as sodium sulfite and sodium meta-bisulfite. The ORP is significantly decreased, but the pH does not change significantly.

## 2.3. Instruments

### 2.3.1. GFAAS

Graphite Furnace Atomic Adsorption Spectrometer (GFAAS, PerkinElmer AA Analyst 800 model) equipped with an electrodeless discharge lamp was used for the analysis of arsenic. The GFAAS can measure most metallic elements with 20 to 1000 times better sensitivities than using conventional flame techniques. This increased sensitivity results from an increase in atom density within a furnace as compared to flame atomic adsorption. Many elements can be detected at concentration as low as 1.0 μg/L. The GFAAS is based on the same principle as flame atomic adsorption. First, an element is atomized in a graphite tube at high temperature. The light beam is directed through atomization area to a slit, and a detector measures the amount of light absorbed by the atomized element as a signal. Each metal has its own characteristic adsorption wavelength. The selected wavelength for arsenic is 193.7 nm with a spectral slit width of 0.7 nm. The peak area was measured as a signal.

There are three or more stages in an atomization process. First stage dries sample at low temperature. The second stage destroys organic compounds and volatilizes other matrix components at an intermediate temperature. Finally, high heat is applied to the tube and atomizes the element being measured. Additional stage is added to clean and cool the tube between samples.

| Step # | Temp °C | Ramp Time (sec) | Hold Time (sec) | Internal Flow | Reading |
|---|---|---|---|---|---|
| 1 | 110 | 1 | 30 | 250 | / |
| 2 | 130 | 15 | 30 | 250 | / |
| 3 | 1200 | 10 | 20 | 250 | / |
| 4 | 2000 | 0 | 5 | 0 | X |
| 5 | 2450 | 1 | 3 | 250 | / |

Table 5. Furnace Program for Arsenic Analysis

Matrix modification can be useful in minimizing interference and background signal. Chemical modifiers generally modify relative volatility of matrix and metal. Some modifiers enhance matrix removal, which results in the isolation of the target metal. For arsenic measurement, matrix modifier was prepared by dissolving 0.004 g of $PdCl_2$ in 0.1 ml of concentrated HCl. This solution was mixed with a solution prepared by dissolving 0.020 g of ammonium paratungstate $(NH_4)_{10}H_2W_{12}O_{24}$ and 0.400 g of citric acid in 5-10 ml of DI water. The resulting solution was brought up to 20 ml with DI water.

Zeeman background correction, which provides accurate background correction, was used for this study. This correction is based on the principle that magnetic field splits the spectral line into two light beams. One is called $\pi$ component and the other called $\sigma$ component. These two light beams have exactly the same wavelength and differ only in the plane of polarization. The $\pi$ line will be adsorbed by both the atoms of the element of interest and by the background caused by broadband adsorption and light scattering of the sample matrix. The $\sigma$ line will be adsorbed only by the background. The subtraction of the signal of the $\sigma$ line from the $\pi$ line will give a signal of the element of interest (Standard Method, 1995).

### 2.3.2. ORP, pH and DO Meter

The ORP, pH and DO were determined with ORP meter (ORP FM1, OAKTON), pH meter (D-12 Model, HORIBA) and DO meter (97-08-00 Model, ORION), respectively.

# 3. BATCH TEST

## 3.1. Arsenate Adsorption

### 3.1.1. As(V) Kinetics Studies

*Sample Preparation :*

Since the regulation for arsenic is 50 ppb, the initial concentration of 100 ppb As(V) was prepared for this test. A standard solution of 1000 ppm was made by adding 0.4161 g of $Na_2HAsO_4 \cdot 7H_2O$ into 100 ml of DI water. 1 ml of 1000 ppm standard solution was added into 100 ml of volumetric flask to make 10 ppm standard solution. 100 ppb solution was prepared by taking 1 ml of 10 ppm solution and diluting it up to 100 ml. A prepared 100 ppb solution was poured into a 160 ml glass bottle and 0.05 g of either plain or treated activated carbon was added to the solution.

Glass bottles were used for the batch test in order to avoid the risk of adsorption onto the container. Moreover, a 160 ml glass bottle was chosen because it has the 60 ml of head space that can help the mixing process. To observe the difference of adsorption kinetics, an optimum amount of 0.05 g of activated carbon was selected. This is because pre-experiments showed that there was no significant difference in adsorption kinetics when the amount of 0.05 g, 0.1 g, or 0.2 g of activated carbon were added into 100 ppb of As(V) solution, respectively (see the appendix).

*Sampling Method :*

The prepared glass bottles were put on a shaker and mixed at 120 rpm for 52 hours. Samples of 2 ml were taken after 2 hours, 6 hours, 16 hours, 28 hours and 52 hours of shaking from each respective bottle during shaking. The parameters of pH, DO, and ORP were measured before and after shaking.

## *Result & Discussion :*

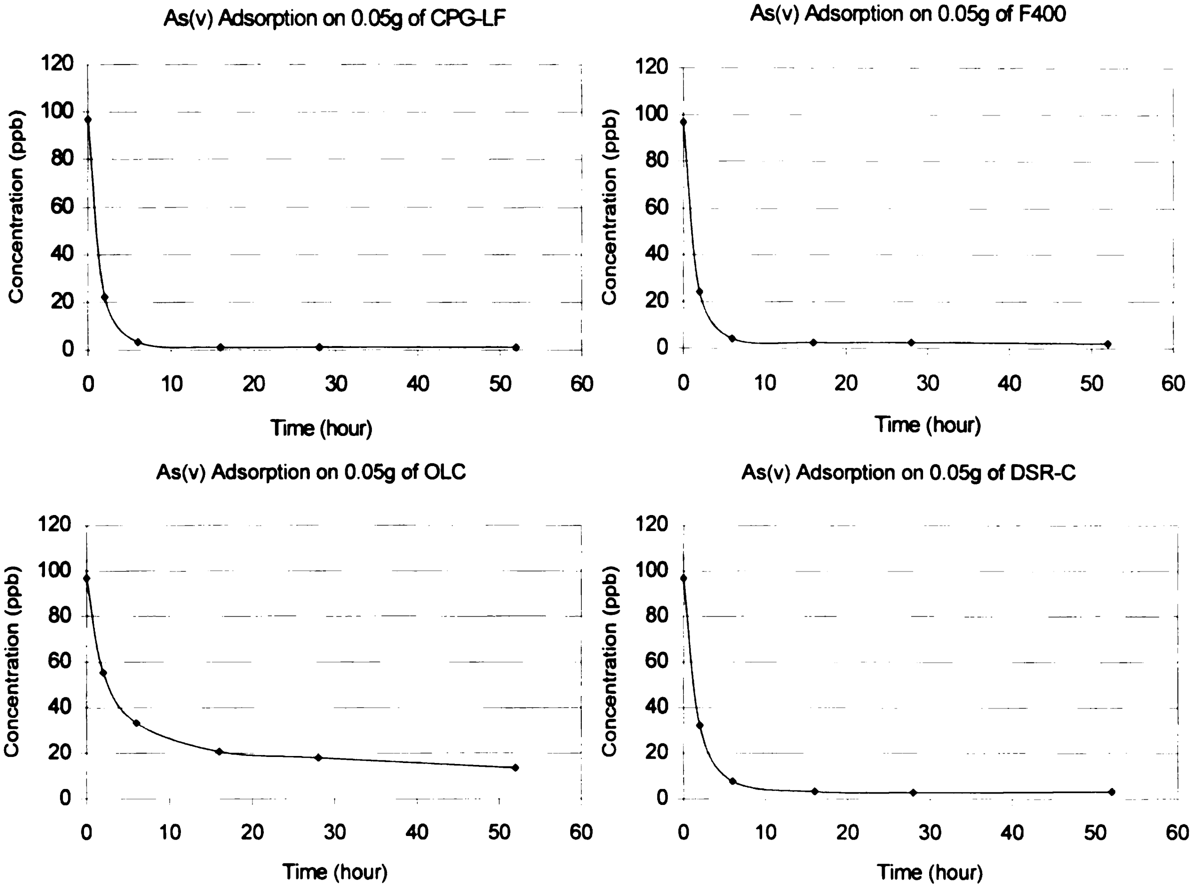

Figure 2. As (V) Adsorption on 0.05 g of Plain Activated Carbon,

pH = 7.2, ORP = 175 mV

CPG-LF, F400, and DSR-C showed good adsorption kinetics for arsenate removal as demonstrated in figure 2. Equilibrium was achieved after 20 hours of shaking with concentration of 1 to 5 ppb. OCL removed less arsenate than other three activated carbons. The adsorption kinetics of treated activated carbons is shown in figure 3.

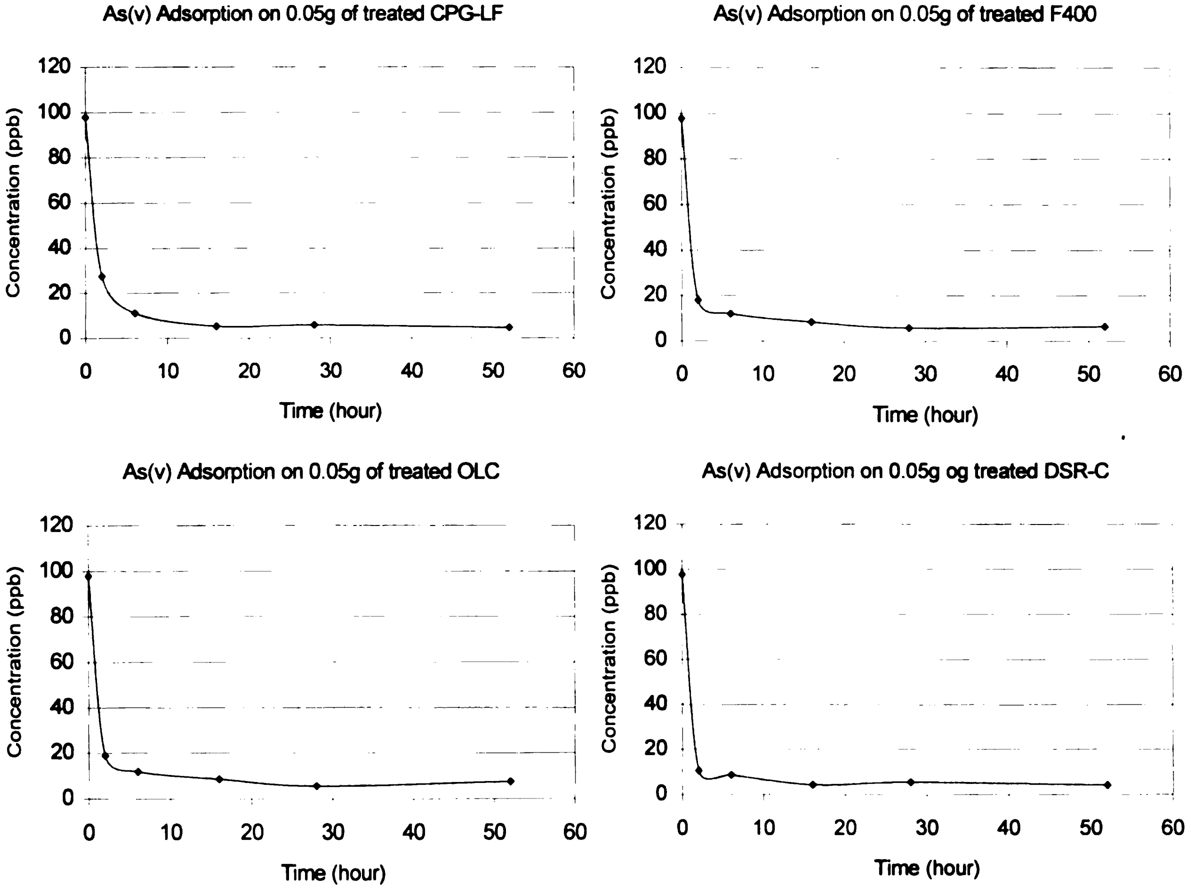

Figure 3. As(V) Adsorption on 0.05 g of Treated Activated Carbon

Treated activated carbon also showed good removal efficiency for arsenate. The adsorption kinetics of OLC was improved by treating with ferrous sulfate. Figure 4 shows the comparison of adsorption kinetics on plain and treated activated carbons.

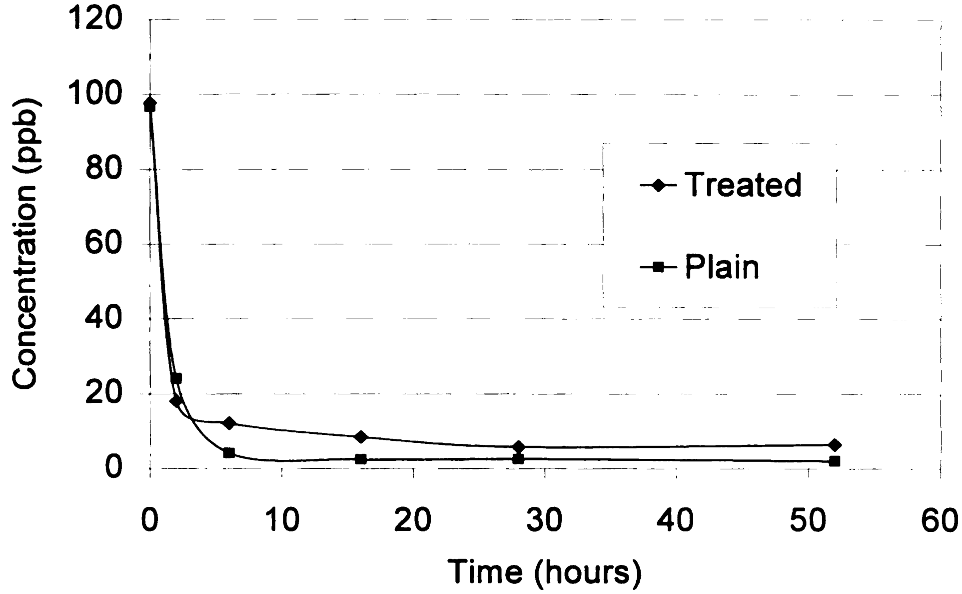

Figure 4. Comparison of Plain and Treated Activated Carbon, Represented by 0.05 g of Plain and Treated F400

After 2 hours of shaking, the concentration of arsenate in solution with treated F400 is slightly lower than that with plain F400. This indicates that the affinity of arsenate for the adsorbent was slightly increased by treating with ferrous sulfate. However, the equilibrium concentration of arsenate in solution with treated adsorbent is slightly higher than that with plain adsorbent. This means the adsorptive capacity of treated activated carbon is less than that of plain activated carbon. It is a reasonable hypothesis that the adsorption sites had been already occupied by ferrous sulfate, so that the adsorptive capacity available for arsenic decreased.

### *Eh-pH Change during Batch Test*

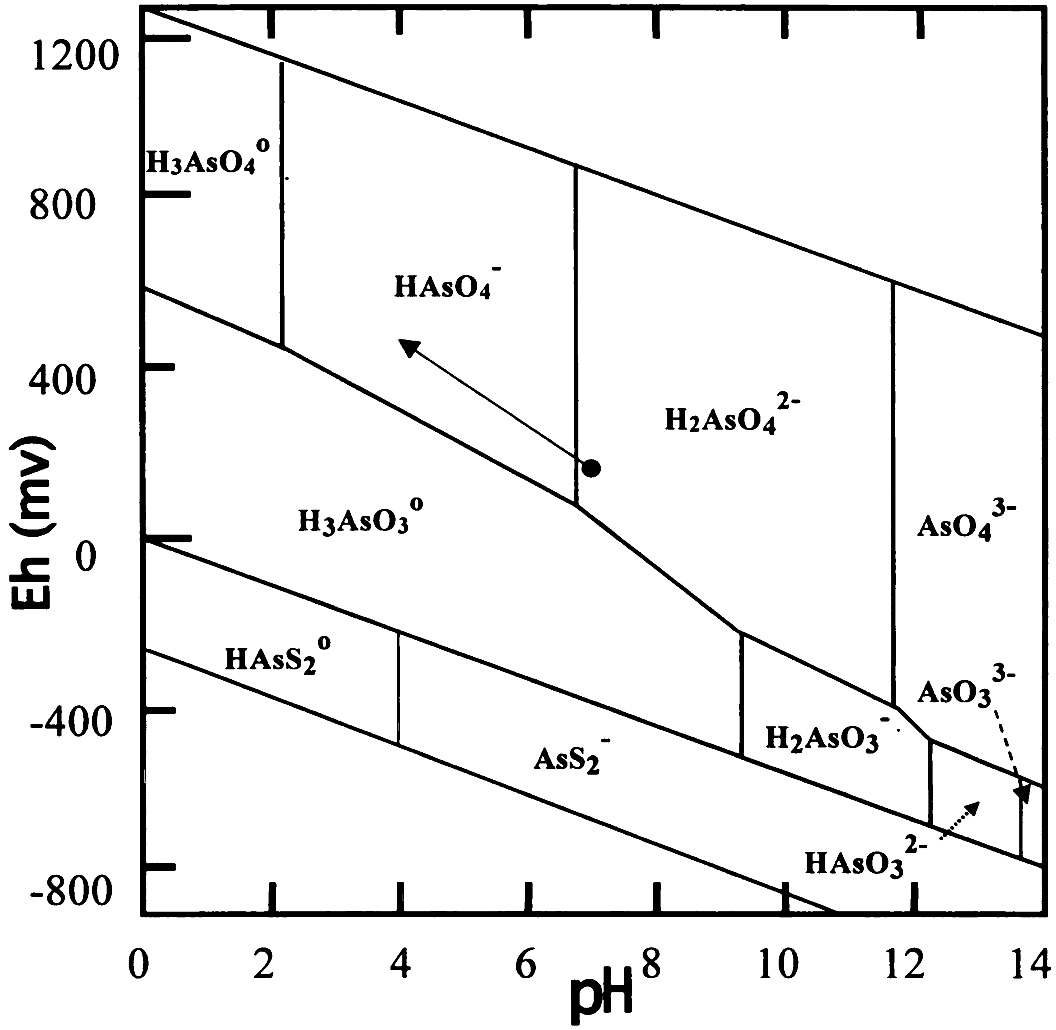

Figure 5. Eh-pH Change during Batch Test, ●——► indicates the Eh- pH Change of Solution Contains Treated DSR-C.

Figure 5 Shows the Eh-pH change of solution during the batch test. The solution contains plain activated carbon did not show any significant change in ORP and pH. However, the ORP and pH were significantly changed in the solution with treated activated carbon. The ORP increased from 170 mV to about 450 mV and pH decreased from 7.2 to about 3.9. It may be because adsorbed ferrous sulfate was dissociated into solution.

### 3.1.2. Adsorption Kinetics Changes

Comparing the kinetics curve of Aug. 2000 with that of Feb. 2001, there is a difference between kinetics curves.

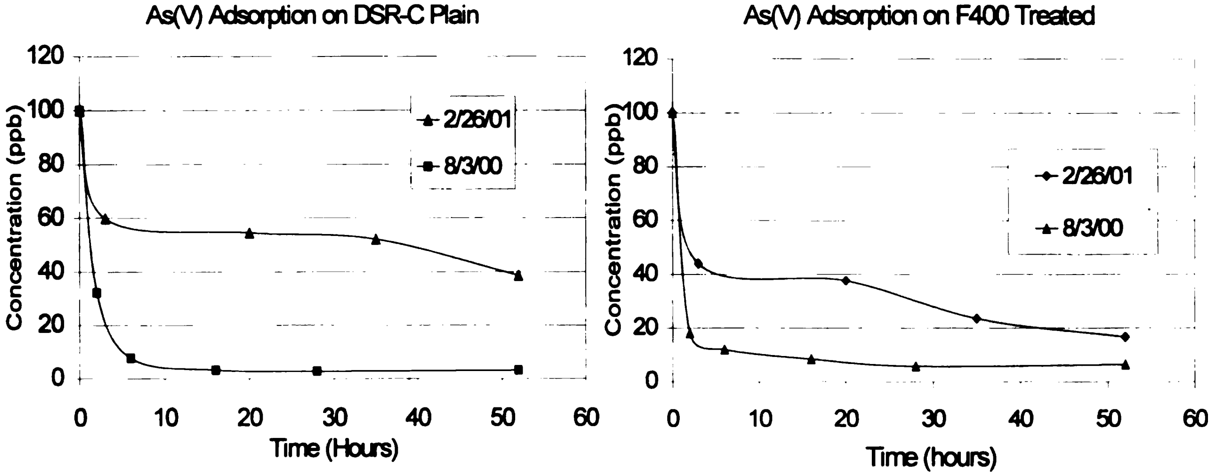

Figure 6. Change of Adsorptive Capacity on Plain DSR-C and Treated F400

As you can see in figure 6, adsorptive capacity on plain DSR-C worsened as time went by (Aug' 00 to Feb' 01). This could be because plain DSR-C was oxidized by air or reacted with moisture in the air while it was kept in the container. The same thing happened in treated activated carbons.

Both treated F400 and treated CPG-LF showed less adsorptive capacity in Feb. 2001 than in Aug. 2000.

### 3.1.3. As(V) Isotherm

*Sample Preparation*

The amount of activated carbon was fixed at 0.05 g. The optimum initial concentration of arsenate was chosen, so that the equilibrium concentration can be achieved in the range of 0 to 100 ppb. Judging from the kinetics curve, solutions with the initial concentrations of 1000 ppb, 800 ppb, 600 ppb, 400 ppb, and 200 ppb were prepared for plain CPG-LF and plain F400. The solutions with initial concentrations of 600 ppb, 500 ppb, 400 ppb, 300 ppb, and 200 ppb were chosen for plain OLC since it showed less adsorption kinetics. The isotherm for plain DSR-C was not performed because its adsorptive kinetics had already changed. The initial concentration of 500 ppb, 400 ppb, 300 ppb, and 200 ppb were prepared for treated OLC and treated DSR. The isotherm for treated F400 and treated CPG was not performed for the same reason.

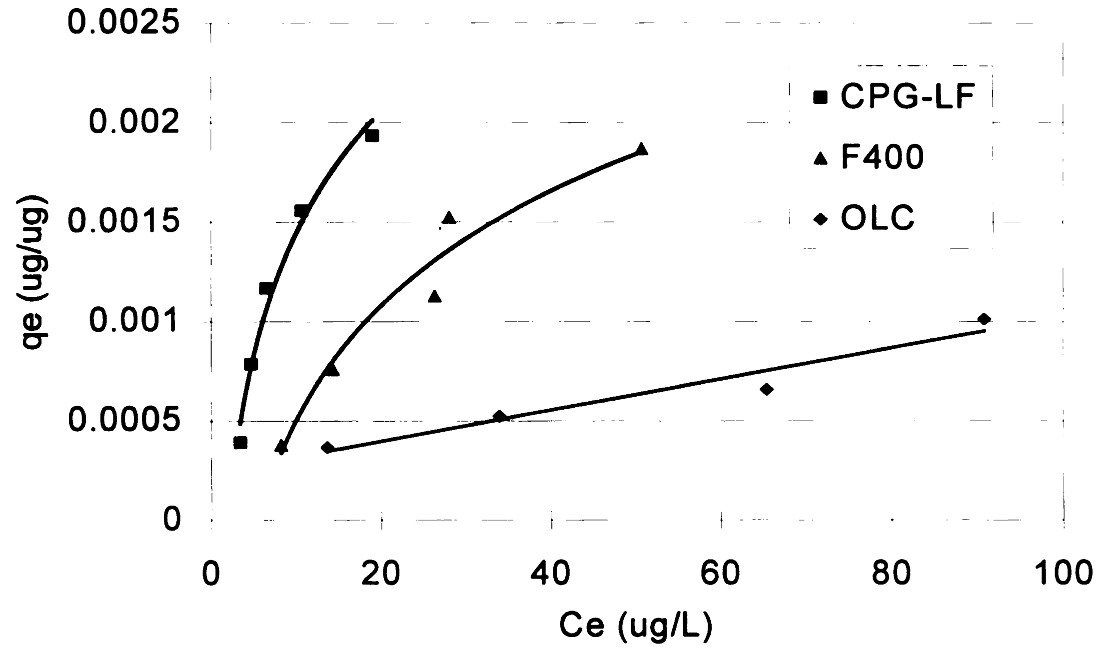

Figure 7. Isotherm of Plain Activated Carbon for As(V) at 23 °C

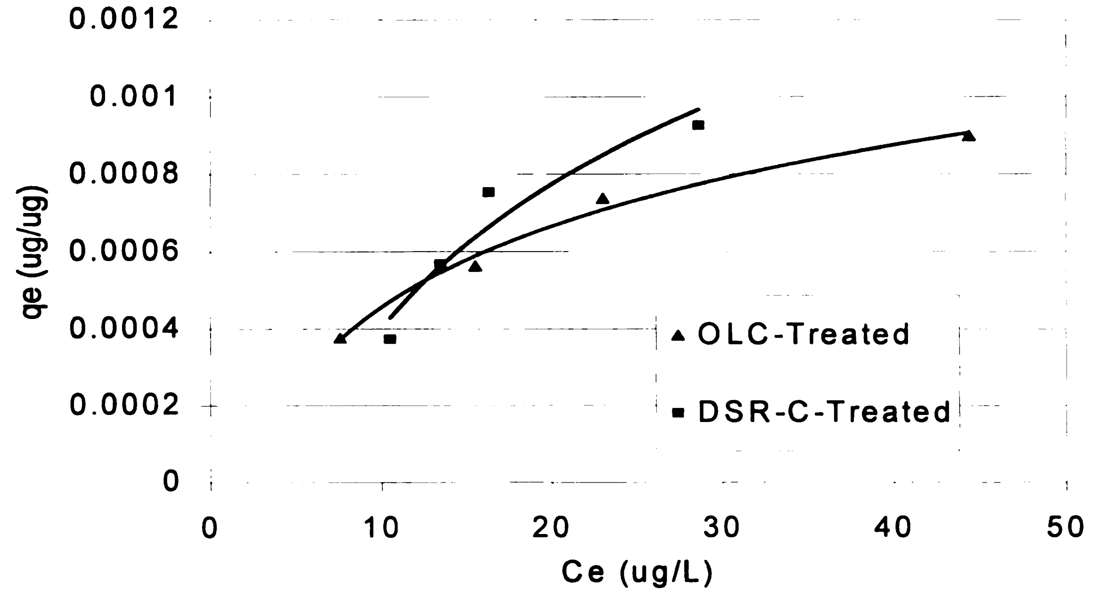

Figure 8. Isotherm of Treated Activated Carbon for As(V) at 23 °C

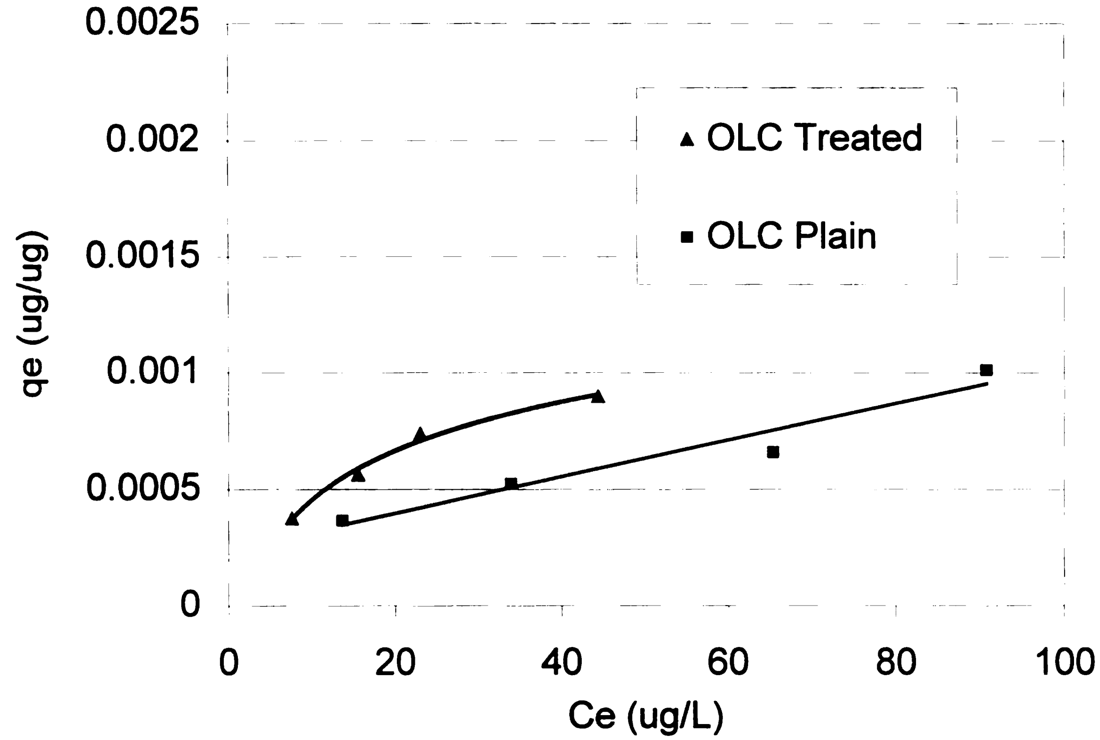

Figure 9. Comparison of Plain OLC with Treated OLC

Plain CPG-LF showed the best isotherm curve as shown in figure 7. From figure 7, it is found that 1.0 g of plain CPG-LF can adsorb 2.0 mg of As(V) at equilibrium concentration of 20 ppb. It means that 1.0 g of plain CPG-LF can treat 20 to 25 L of the contaminated water with influent concentration of 100 ppb until the effluent concentration is over 20 ppb, if sufficient contact time is given. In the same manner, 1.0 g of plain F400 can treat 11 to 13 L of wastewater that contains 100 ppb of influent concentration until the effluent concentration reaches 20 ppb. From the laboratory test, it was found that 1 g of CPG-LF occupied 2.275

$cm^3$. Therefore, if 1 g of CPG-LF is put in the column, it can treat 8,790 to 10,990 bed volumes until the effluent concentration reaches 20 ppb. From the figure 9, it is found that treated OLC has an improved isotherm curve when compared with that of plain OLC, but the difference between these two is not significant.

## 3.2. Arsenite Adsorption

### 3.2.1. As(III) Kinetics Studies

Several experiments were performed to study the adsorption kinetics of arsenite. Each experiment is discussed in the following stage in detail. In each experiment, DI water was pretreated by purging with nitrogen and/or adding reducing agents to keep arsenite in its reduced form at near pH range. The plastic bottle with the capacity of four liters was used for pretreatment. The ORP, DO and pH, which determine whether the arsenite is kept in its reduced form, were carefully monitored and adjusted in this process.

After the optimum surrounding condition for arsenite was achieved by pretreatment, the standard solution of 1000 ppm of As(III) was prepared by dissociating 0.17343 g of $NaAsO_2$ into 100 ml of pretreated DI water. One ml of 1000 ppm standard solution was taken and added into 100 ml of volumetric flask to make 10 ppm standard solution. A solution of 100 ppb was prepared by taking 1 ml of 10 ppm solution and diluting it up to 100 ml. Prepared 100 ppb solution was poured into a 160 ml glass bottle and 0.05 g of either plain or treated activated carbon was added into solution. The prepared glass bottles were mixed well with a shaker for about 50 hours. Four samples were taken from each bottle during shaking. Blanks were prepared to see the variation of pH, DO and ORP during and after shaking.

## a). Conditions Under Eh 40 mV and pH 6.5

*Sample Preparation:*

Four liters of DI water in a plastic bottle was purged with nitrogen gas for two hours. After purging, 3.5 g of sodium meta-bisulfite ($Na_2S_2O_5$) and 1.5 g of sodium sulfite ($Na_2SO_3$) were added to the purged DI water. The change in pH, DO and ORP during this process are summarized in the Table 6.

| | DO (mg/L) | pH | ORP (mV) |
|---|---|---|---|
| Initial Condition of water | 2.88 | 7.24 | 185 |
| After purging with $N_2$ | 0.81 | 7.44 | 185 |
| After addition of Reducer | 0.1 | 6.52 | 40 |
| Before Shaking | 0.11 | 6.48 | 45 |

Table 6. The change of DO, pH and ORP by Pre-Treatment

By this pre-treatment, pH of 6.5 and ORP of 45 mV were achieved, at which the arsenite can be kept in reducing form (see Figure 14).

The standard solution of 1000 ppm of arsenite was prepared by dissociating 0.17343 g of $NaAsO_2$ into 100 ml of the pretreated DI water.

One ml of 1000 ppm standard solution was taken and added to 100 ml of volumetric flask to make 10 ppm standard solution. A solution of 100 ppb was prepared by taking 1 ml of 10 ppm solution and diluting it up to 100 ml. Prepared 100ppb of As(III) solution was poured into a 160 ml glass bottle. This preparation was done under aerobic conditions, so the exposure of the samples to the air was expected.

Then, 0.05 g of plain CPG-LF, F400 and OLC were added into three glass bottles filled with pre-treated solutions, respectively. Four blanks, which have 100 ppb of arsenite and no activated carbons, were prepared. Also four CPG-LF blanks, which have 100 ppb of arsenite and 0.05 g of CPG-LF were prepared. Treated activated carbons were not performed because those adsorbents change the condition of pH and ORP in solution.

*Sampling Method:*

The prepared samples and blanks, a total of 11 bottles, were shaken at 120 rpm for 50 hours. Samples of 2 ml were taken from each bottle after 2 hours, 6 hours, 18 hours and 50 hours of shaking, respectively. The pH, DO and ORP of blank and CPG-LF blank solutions were measured after 2 hours, 6 hours, 18 hours and 50 hours of shaking, respectively.

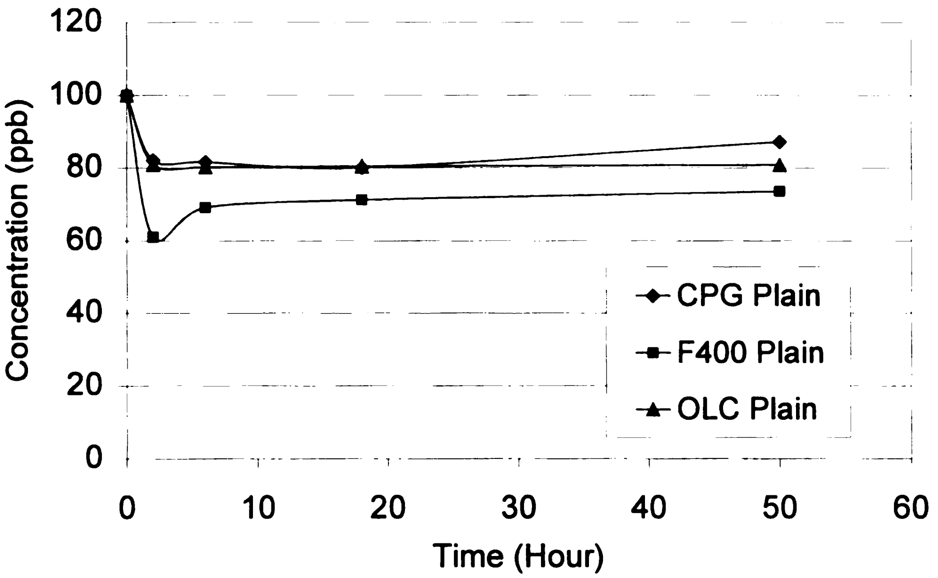

Figure 10. As(III) Adsorption on 0.05 g of Plain Activated Carbons

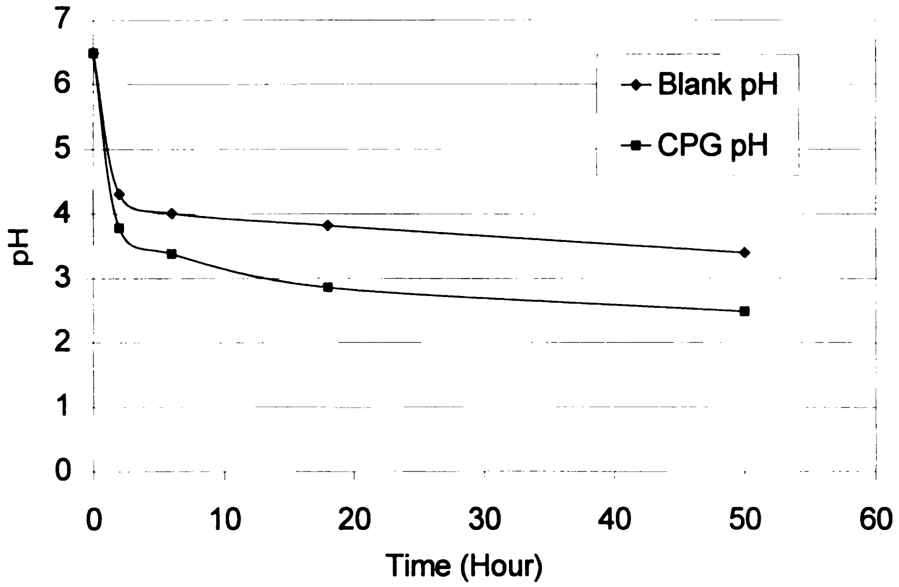

Figure 11. The pH Change of Blank and CPG-LF Blank During Shaking

Figure 11 shows the change of pH in the blank solution and in the solution which contains 0.05 g of CPG-LF. The pH of the blank solution decreased from 6.5 to 3.5 during shaking. This pH reduction was attributed to the reaction $SO_3^{2-} + O_2 \Rightarrow SO_4^{2-}$. The pH of the solution, which contains 0.05 g of CPG-LF, showed a lower pH (pH 2.5) than that of the blank solution. It is hypothesized that the sodium ion ($Na^+$) was adsorbed onto CPG-LF, or the acid that is used in the manufacturing process of CPG-LF was leached into solution. It is also one possible hypothesis that the oxygen which are contained in activated carbons are dissolved into solutions and lowered pH by accelerating the reaction of $2SO_3^{2-} + 2O_2 \Rightarrow 2SO_4^{2-}$.

From Fig.10, it was found that arsenite, which was present in the solution as $H_3AsO_3$ in this pH range (6.5 to 2.5), was not adsorbed effectively onto plain activated carbons. The concentration of arsenite in solution became stable at about 80 ppb after 20 hours of shaking. It means that 80% of arsenite was not adsorbed and remained in the solution.

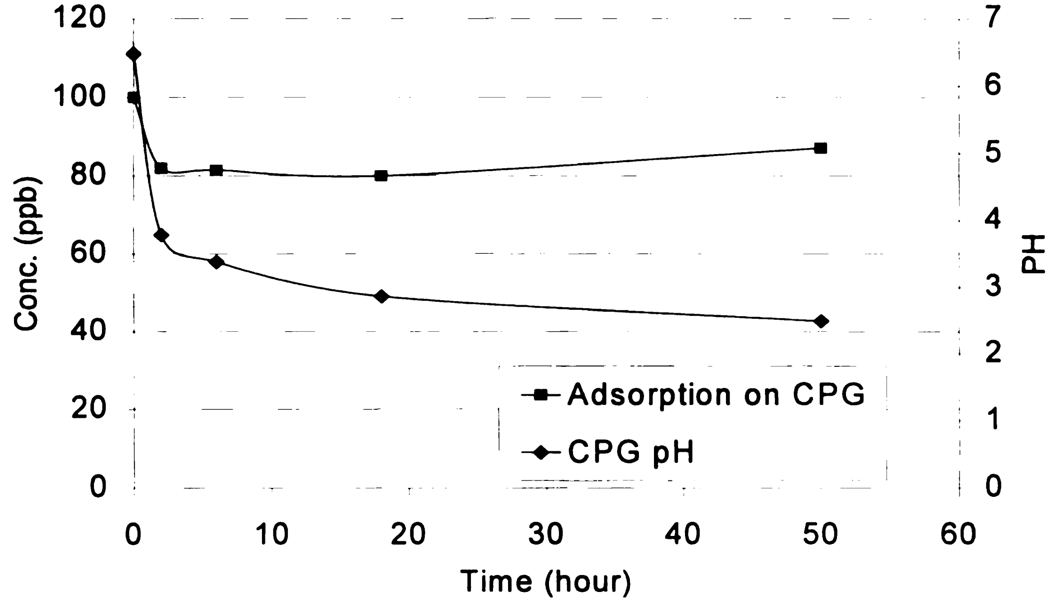

Figure 12. The pH Effect on Arsenite Adsorption Kinetics, 0.05 g of CPG

Figure 12 shows the pH effect on arsenite adsorption kinetics. First 2 hours, arsenite was slightly adsorbed onto the activated carbon. This small amount of adsorption can be explained by referring to Eh-pH diagram (see Fig.14). Under the initial condition of the solution (pH 6.5, ORP 40), a small proportion of arsenic would exist as arsenate since the condition of the solution is close to the boundary of arsenite and arsenate. It is considered that the arsenate in solution was adsorbed onto activated carbon in the first two hours. The pH of the solution decreased down to 2.5 with time, and the concentration of arsenite in solution was maintained near 80 ppb though it showed slight desorption.

There was no significant difference in adsorption kinetics in the pH range of 6.5 to 2.5. This is because in this pH range (6.5-2.5) arsenite is stable as $H_3AsO_3$.

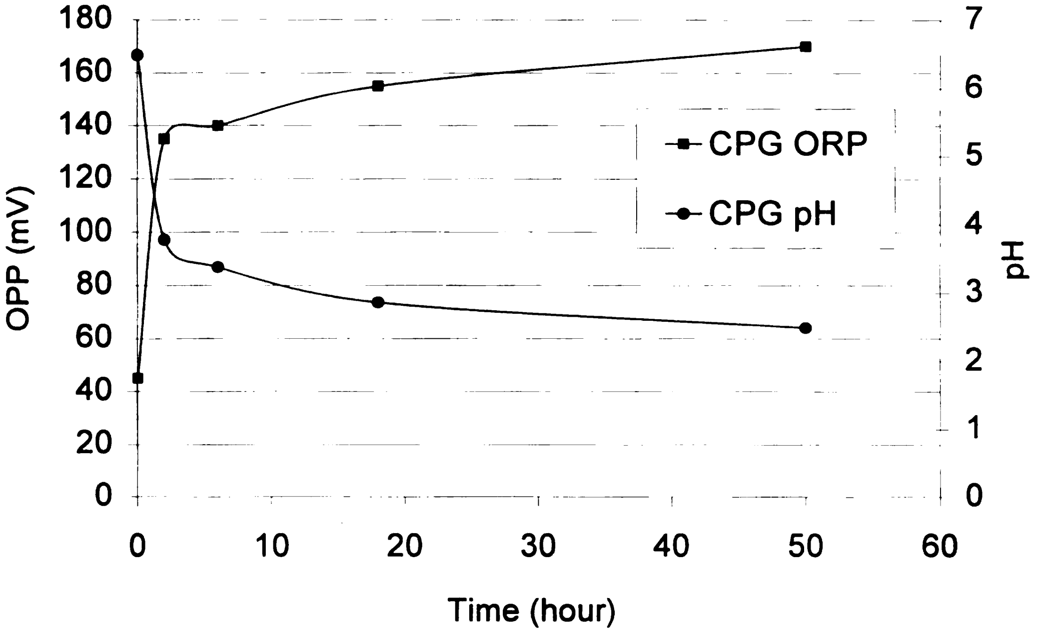

Figure 13. The Relation of pH and ORP

Figure 13 shows that the ORP value increased as the pH decreased. As mentioned before, the conversion of $SO_3^{2-}$ to $SO_4^{2-}$ during shaking caused the pH to decrease. The increase of ORP value was also attributed to this conversion, especially the increase of sulfate and hydrogen ion concentration.

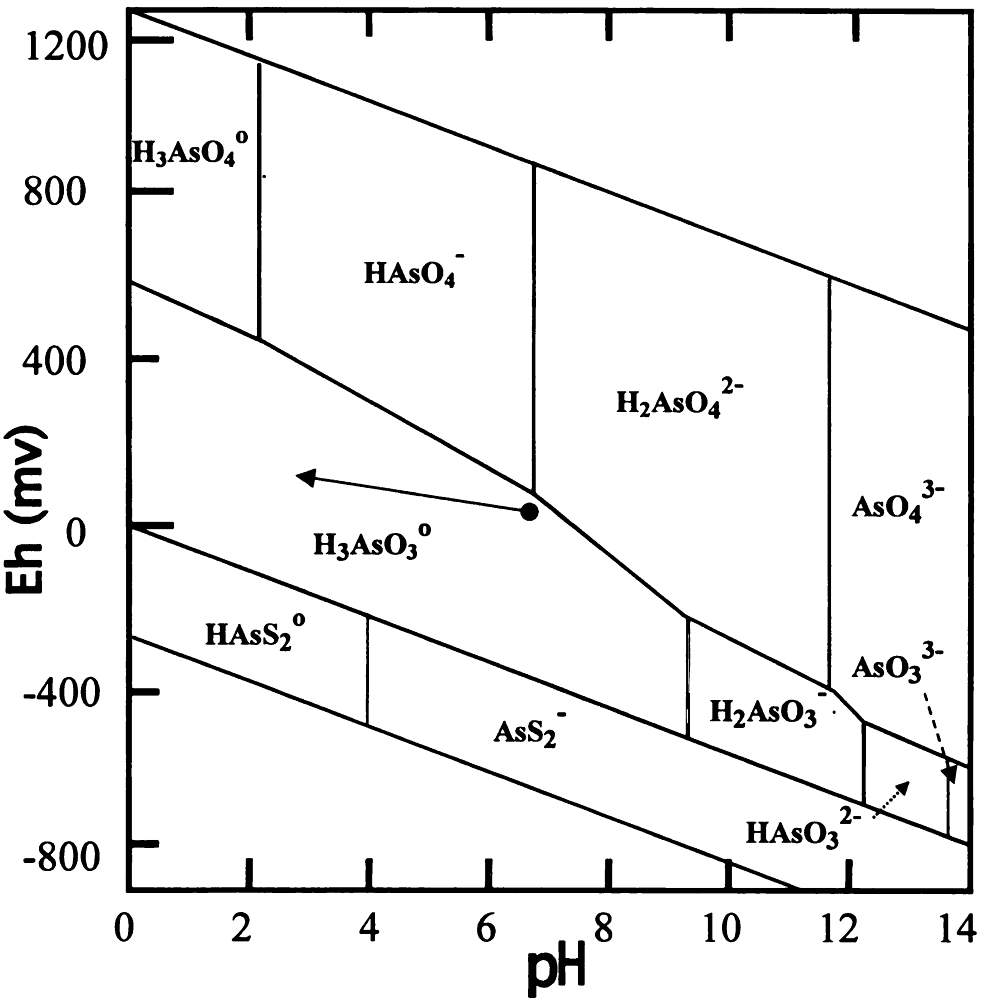

Figure 14. The Shift of pH and ORP during Shaking

The arrow in Fig.14 shows the change of pH and ORP in the solution during shaking. The arrow is directed toward the center of the domain. The more center the condition, the more predominant the species would be. It means that arsenite was the strong predominant species and stable in this solution at the end of shaking.

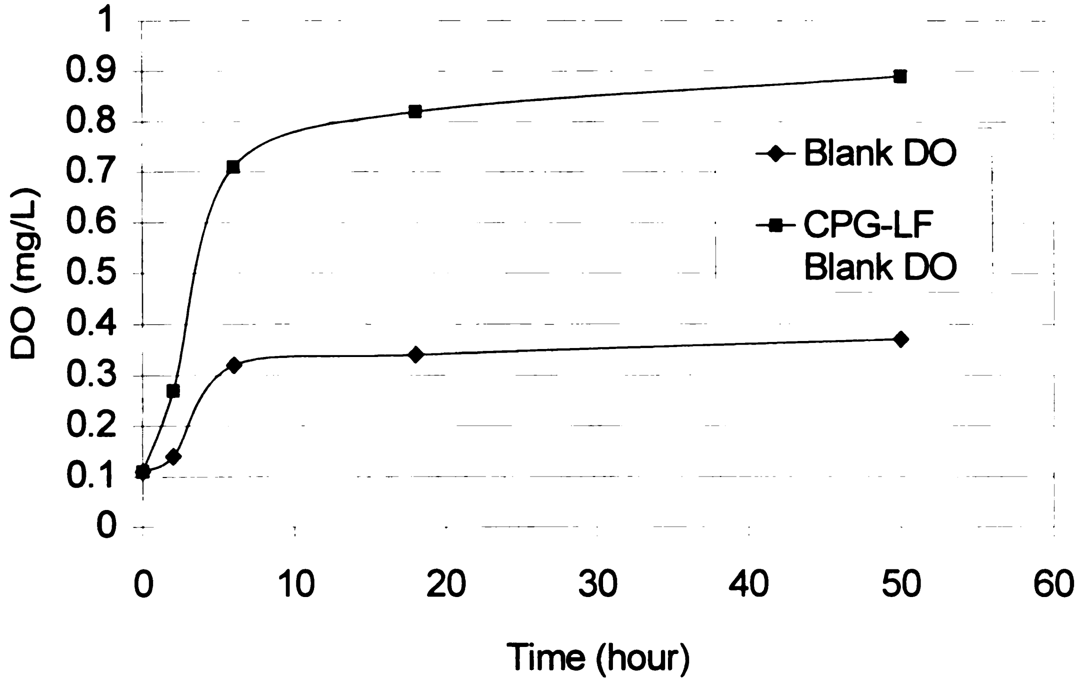

Figure 15. The Change of Dissolved Oxygen in the Solution

From Fig.15, it was found that DO had increased from 0.1 to 0.4 mg/L in the blank solution during shaking. The increase of the dissolved oxygen was derived from the air in the headspace of the glass bottle. DO in the solution that contains 0.05 g CPG-LF increased from 0.1 to 0.8 mg/L. This difference indicates that additional oxygen was introduced in the solution which contains CPG-LF. It is considered that activated carbons usually contain air and the air in activated carbon dissolved into solution. Indeed, air bubbles could be seen when the activated carbon was added to the solution. Dissolved oxygen must be consumed when the reaction $SO_3^{2-} + O_2 \Rightarrow SO_4^{2-}$ proceeds.

### b). Conditions Under Eh 90mV and pH 5.0

In the previous experiment, the pH and ORP of solution changed significantly due to the reaction of the added reducing agent with oxygen. To keep the condition of the solution constant, another reducing agent was added into solution.

*Sample Preparation:*

Four liters of DI water in a plastic bottle was purged with nitrogen gas for two hours. After purging, 3.5 g of sodium meta-bisulfite ($Na_2S_2O_5$) and 1.5 g of sodium thiosulfate ($Na_2S_2O_3$) were added into the purged DI water. The change of pH, DO and ORP in this process are summarized in Table 7.

| | DO (mg/L) | pH | ORP (mV) |
|---|---|---|---|
| Initial Condition of water | 2.51 | 7.17 | 170 |
| After purging with $N_2$ | 0.67 | 7.42 | 165 |
| After addition of Reducer | 0.34 | 5.01 | 90 |
| Before Shaking | 0.32 | 5.03 | 85 |

Table 7. The change of DO, pH and ORP by Pre-Treatment

By this pre-treatment, pH of 5.0 and ORP of 85 mV were achieved, at which the arsenite can be kept in a reduced form.

The solution of 100 ppb of arsenite was prepared by using the pretreated DI water in the same manner as in the previous experiment. Pre-treated solution was put into glass bottles. Then, 0.05 g of CPG-LF, F400 and OLC were added into three glass bottles, respectively. Four blanks, which have 100 ppb of arsenite and no activated carbons, were prepared. Also four CPG-LF blanks, which have 100 ppb of arsenite and 0.05 g of CPG-LF were prepared. Treated activated carbons were not performed because of the same reason mentioned earlier.

*Sampling Method:*

The prepared samples and blanks, the 11 bottles, were shaken at 120 rpm for 50 hours. Two ml of each sample was taken from each bottle after 2 hours, 8 hours, 20 hours and 50 hours of shaking. The pH, DO and ORP of blank and CPG-LF blank solutions were measured after 2 hours, 8 hours, 20 hours and 50 hours of shaking, respectively. The pH, DO and ORP of the solutions which contain F400 and OLC were also measured before and after shaking (not at intermediate times).

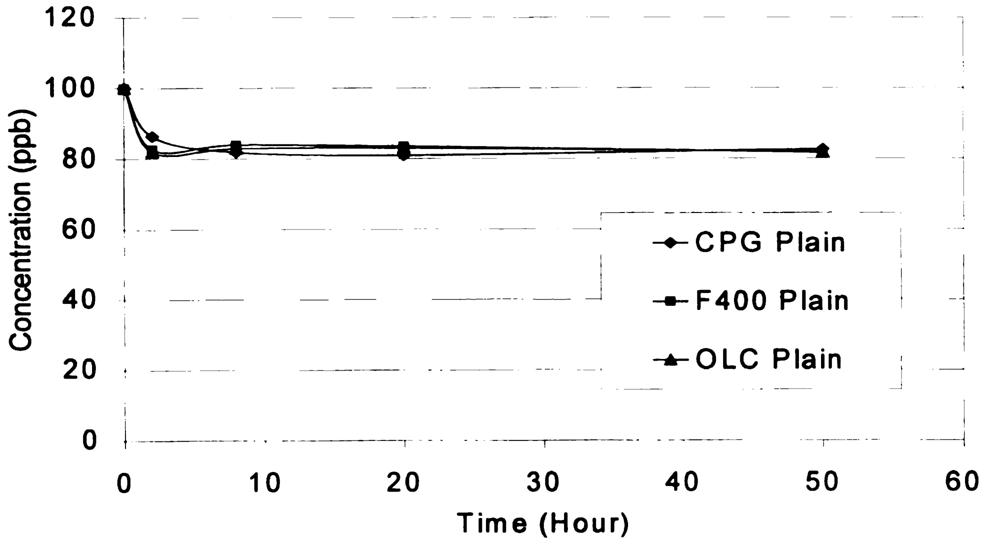

Figure 16. As(III) Adsorption on 0.05 g of Plain Activated Carbons

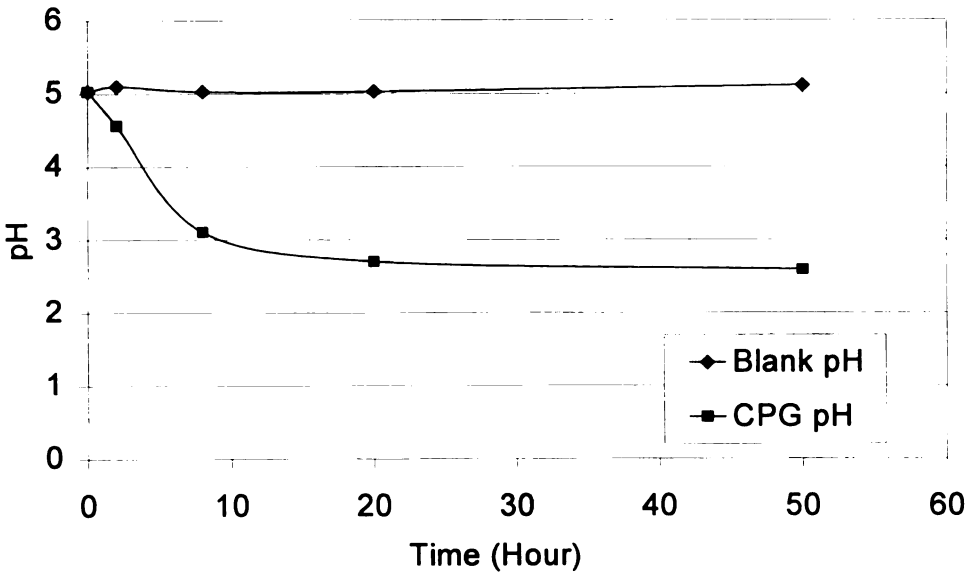

Figure 17. The pH Change in Solution during Shaking

Figure 17 shows the change of the pH in the solution during shaking. The pH of the blank solution was kept around 5.0. This is due to the characteristics of sodium thiosulfate in solution. It takes time for sodium thiosulfate to ionize in solution. It means that the reaction $Na_2S_2O_3 \Rightarrow 2Na^+ + S_2O_3^{2-}$ is very slow. Shaking accelerates this reaction and the pH of the solution increases providing sodium ions into solution. The reactions $2S_2O_3^{2-} + 3O_2 \Rightarrow 4SO_3^{2-}$ and $2SO_3^{2-} + 2O_2 \Rightarrow 2SO_4^{2-}$ are also slow. However, the shaking also enhances the kinetics of these reactions and the pH in the solution decreases. Since the reaction $Na_2S_2O_3 \Rightarrow 2Na^+ + S_2O_3^{2-}$ limits the available $S_2O_3^{2-}$, shaking sodium thiosulfate itself increases the pH in solution (see the appendix). The co-existing sodium meta-bisulfite decreases pH due to the reaction $2S_2O_5^{2-} + 3O_2 \Rightarrow 4SO_4^{2-}$. Both effects on pH were canceled out and the pH of the solution was kept constant.

Unlike blank solution, the pH decreased remarkably in the solution contains 0.05 g of CPG-LF. It is hypothesized that the sodium ion ($Na^+$) was adsorbed onto CPG-LF, or the acid that is used in the manufacturing process of CPG-LF was leached into solution. However, the other solutions containing 0.05 g of F400 and OLC, which are not treated by acid in the manufacturing process, showed almost the same pH values after 50 hour of shaking (pH 2.48 and 2.67, respectively). Therefore, the latter hypothesis is not convincible. Another hypothesis suggests that the oxygen, which is contained in activated carbon, is dissolved into solution and accelerated the reaction of $2SO_3^{2-} + 2O_2 \Rightarrow 2SO_4^{2-}$.

Figure 16 showed almost the same result as the previous experiment. Arsenite in solution was not removed effectively by the plain activated carbons. The solution reached the equilibrium concentration of about 80 ppb after 10 hours of shaking.

### c). 0.20 g of A.C. Under Eh 90 mV and pH 5.0

To observe the better adsorption kinetics of arsenite, 0.20 g (four times) of plain activated carbons were added to the solution treated in the same manner as experiment b). The following is the result.

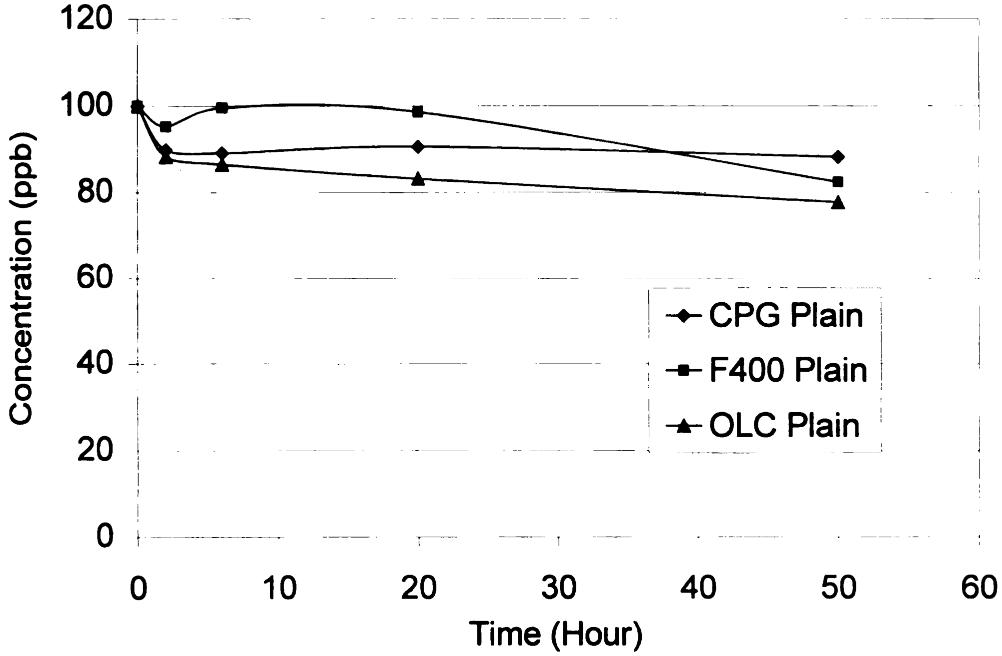

Figure 18. As(III) Adsorption Kinetics on 0.20 g of Plain Activated Carbons

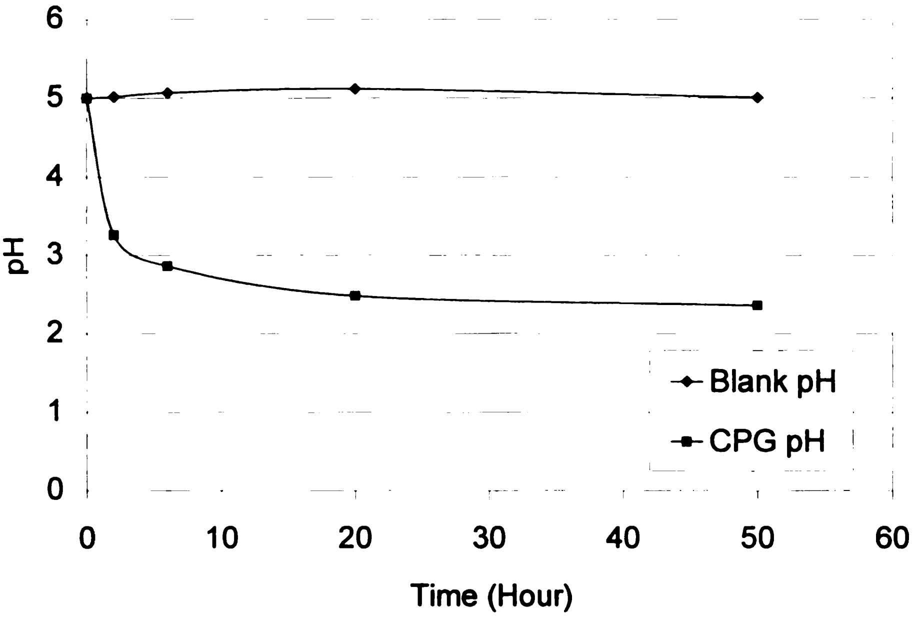

Figure 19. The pH Change in Solution during Shaking

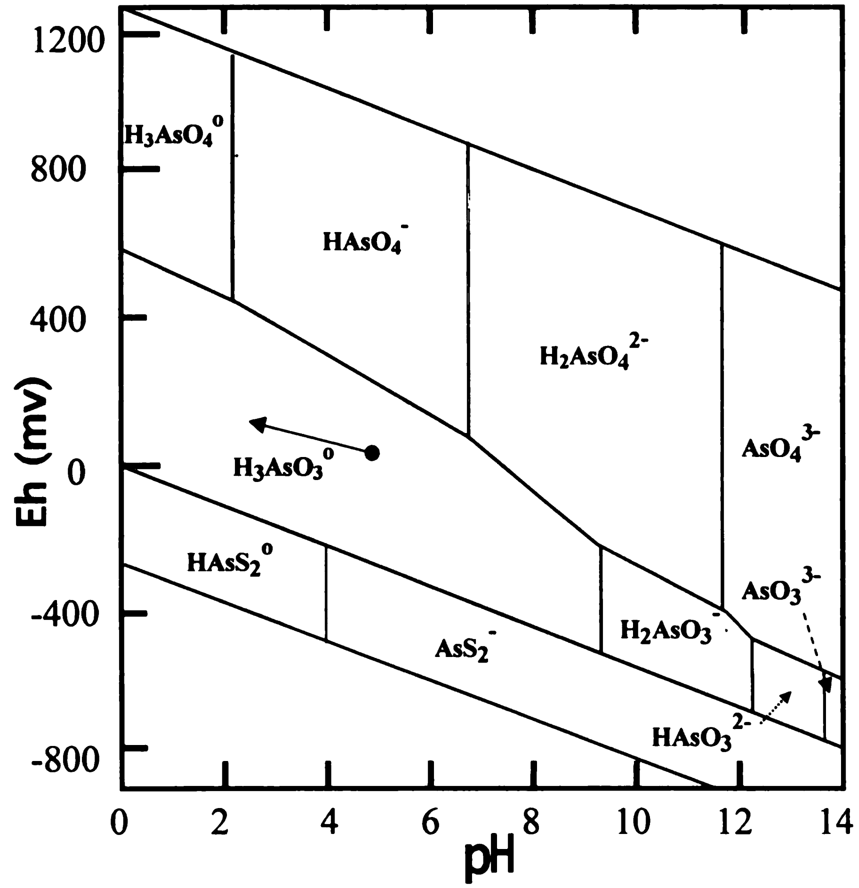

Figure 20. The Shift of pH and ORP during Shaking

Figure 19 shows that the pH of the solution containing 0.20 g of CPG decreased drastically in the first 5 hours compared to the solution containing 0.05 g of CPG-LF. It is hypothesized that the mass of activated carbon was four times larger than 0.05 g and approximately four times the oxygen contained in activated carbon was dissolved into solution. It accelerated the reaction of $2SO_3^{2-} + 2O_2 \Rightarrow 2SO_4^{2-}$ and lowered the pH. Adsorption of the sodium ion ($Na^+$) onto CPG-LF is still a possible hypothesis.

Figure 18 shows that the arsenite was not adsorbed effectively onto 0.20 g of plain activated carbons. There was no significant difference in adsorption kinetics between 0.05 g and 0.20 g of activated carbon in solution. It is considered that chemical attraction between arsenite and activated carbon is weak because arsenite exists as a neutral form $H_3AsO_3$ and stable in this pH range (see Figure 20). There is another possibility that co-existing ions such as sulfate effect on the adsorption of arsenite.

Since arsenite is not adsorbed onto both 0.05 g and 0.20 g of activated carbon, it was impossible to obtain an isotherm curve, which is the relation of mass of adsorbate per unit mass of adsorbent with the equilibrium concentration.

### d). No Reducer

To eliminate the effect of the reducing agent on adsorption kinetics of arsenite, DI water was treated only by purging with nitrogen. Since the oxidation rate of arsenite with dissolved oxygen is very slow, arsenite is supposed to be kept in its reduced form for a certain period. The oxidation rate is also dependent on the concentration of dissolved oxygen, so removal of oxygen by the pre-treatment process will be effective to keep arsenic in its reduced form.

*Sample Preparation :*

Four liters of DI water in a plastic bottle was purged with nitrogen gas for two hours. The solution of 100 ppb of arsenite was prepared by using the pretreated DI water in the same manner as in the previous experiment. Pre-treated solution was put into glass bottles. Then, 0.05 g of plain CPG-LF, plain F400, plain OLC, treated DSR-C and treated OLC were added to five glass bottles, respectively. This process was done under aerobic condition, so the exposure of the samples to the air was expected. The change of pH, DO and ORP in the preparing process are summarized in Table 8.

| | DO (mg/L) | pH | ORP (mV) |
|---|---|---|---|
| Initial Condition of water | 4.51 | 7.37 | 180 |
| After purging with $N_2$ | 0.78 | 7.42 | 175 |
| Before Shaking | 2.05 | 7.54 | 175 |

Table 8. The change of DO, pH and ORP by Pre-Treatment

*Sampling Method:*

The prepared samples were mixed with shaker at 120 rpm for 52 hours. Two ml of each sample was taken from each bottle after 6 hours, 18 hours, 30 hours and 52 hours of shaking. The pH, DO and ORP of each solution were measured before and after shaking (not at intermediate times).

*Results & Discussion :*

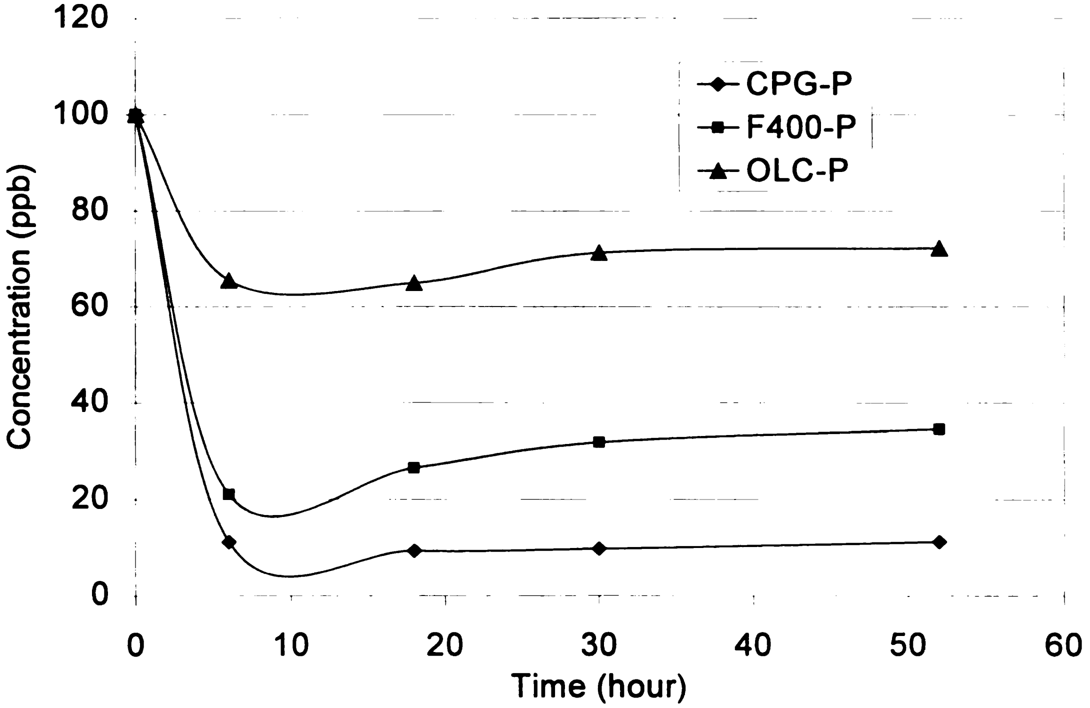

Figure 21. As(III) Adsorption on 0.05 g of Plain Activated Carbons without Reducing Agent, pH 7.5, ORP=175

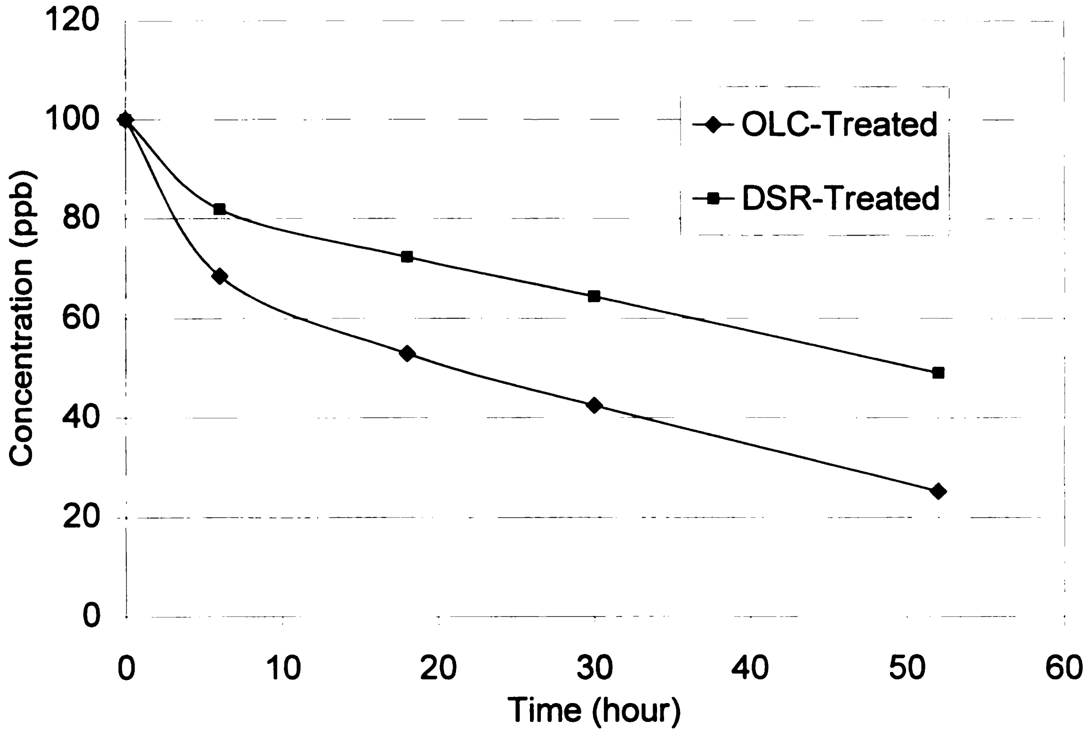

Figure 22. As(III) Adsorption on 0.5 g of Treated Activated Carbons without Reducing Agent

Figure 21 shows the adsorption kinetics of arsenite onto 0.05 g of plain activated carbons. There are significant differences between adsorption kinetics of the three plain activated carbons. OLC plain did not adsorb arsenite effectively, whereas F400 plain adsorbed arsenite by 70%. CPG-LF plain appeared to be the best adsorbent for arsenite. CPG-LF plain removed 90% of arsenite in this experiment. These differences are attributed to the oxidation ability of each activated carbon. The ability of oxidation is dependent on the amount of oxygen contained by the activated carbons. It is possible that CPG-LF contained a larger amount of oxygen than F400 and OLC, and dissolved oxygen released from activated carbon could oxidize arsenite to arsenate, and formed arsenate was effectively removed. There was no significant difference in the pH or ORP between before and after shaking.

Figure 22 shows the adsorption kinetics of arsenite onto 0.05 g of treated activated carbons. These kinetics are definitely different from the kinetics of plain activated carbons. The arsenite in solution was gradually removed by treated activated carbon, whereas most of arsenite was removed by plain activated carbon in the first ten hours. This difference is derived from the difference in the oxidation process between plain and treated activated carbons. This is explained by referring to Table 9 and Figure 23.

| | pH | DO (mg/L) | ORP (mV) |
|---|---|---|---|
| CPG-P | 7.26 | 4.28 | 180 |
| F400-P | 7.32 | 3.8 | 180 |
| OLC-P | 7.36 | 4.83 | 175 |
| OLC-Treated | 4.03 | 4.8 | 355 |
| DSR-Treated | 4.11 | 4.98 | 360 |

Table 9. The pH, ORP, and DO of solutions after 52 Hours of Shaking

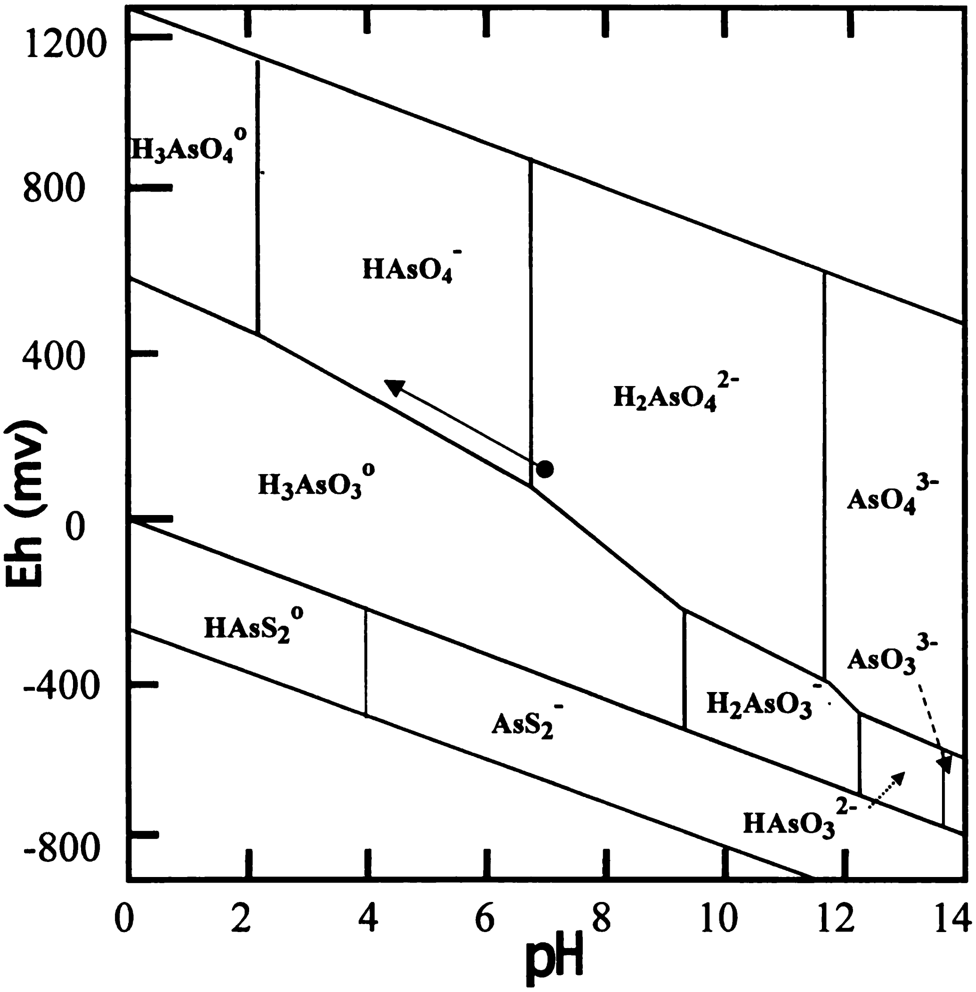

Figure 23. Shift of pH and ORP during Shaking

From Table 9 and Figure 23, it is observed that the pH of the solution with treated activated carbon decreased to 4.1 and the ORP increased to 360 mV. It is presumed that the adsorbed ferrous sulfate was released from the treated activated carbons into solution and changed the condition of the solution. This change of the condition in solution could make the oxidation rate slow compared to the solution with plain activated carbons.

From the experiments a), b) and c), it is understood that arsenite itself can not be removed effectively by activated carbons. However, it was turned out that the removal of arsenite is possible using activated carbon by oxidizing arsenite to arsenate. In experiments a), b) and c), the released oxygen from activated carbons was consumed by reducing agents, and arsenite itself was not oxidized. However, experiment d) showed that arsenite can be oxidized by the oxygen released from activated carbons when there is no reducing agent in the solution.

## 3.3. pH Effect on Adsorption

The pH effect on arsenate adsorption was observed using 0.05 g of plain CPG-LF. The final volume of 100 ml of 100 ppb As(V) solutions were prepared by adding either hydrochloric acid or sodium hydroxide into solution to adjust the pH. Prepared solutions were poured into 160 ml glass bottles and 0.05 g of plain CPG-LF was added to each solution. Prepared bottles were put on a shaker and mixed at 120 rpm for 40 hours until equilibrium condition was obtained. The equilibrium concentration, pH and ORP were measured by using GFAAS, pH meter and ORP meter, respectively. The following is the result.

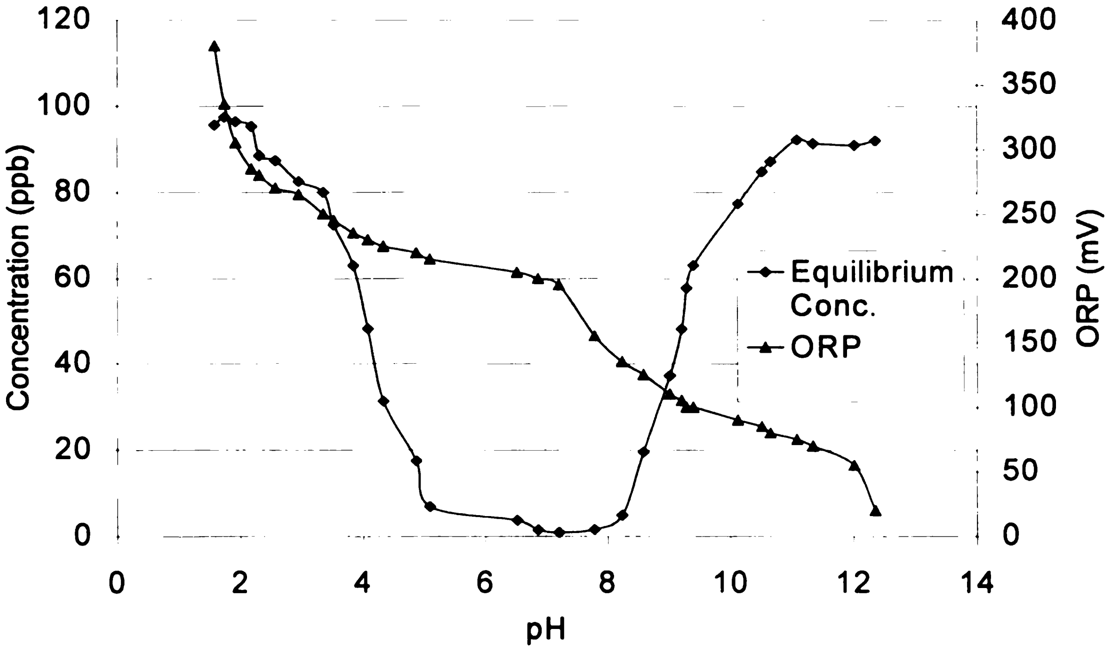

Figure 24. The pH Effect on Arsenate Adsorption

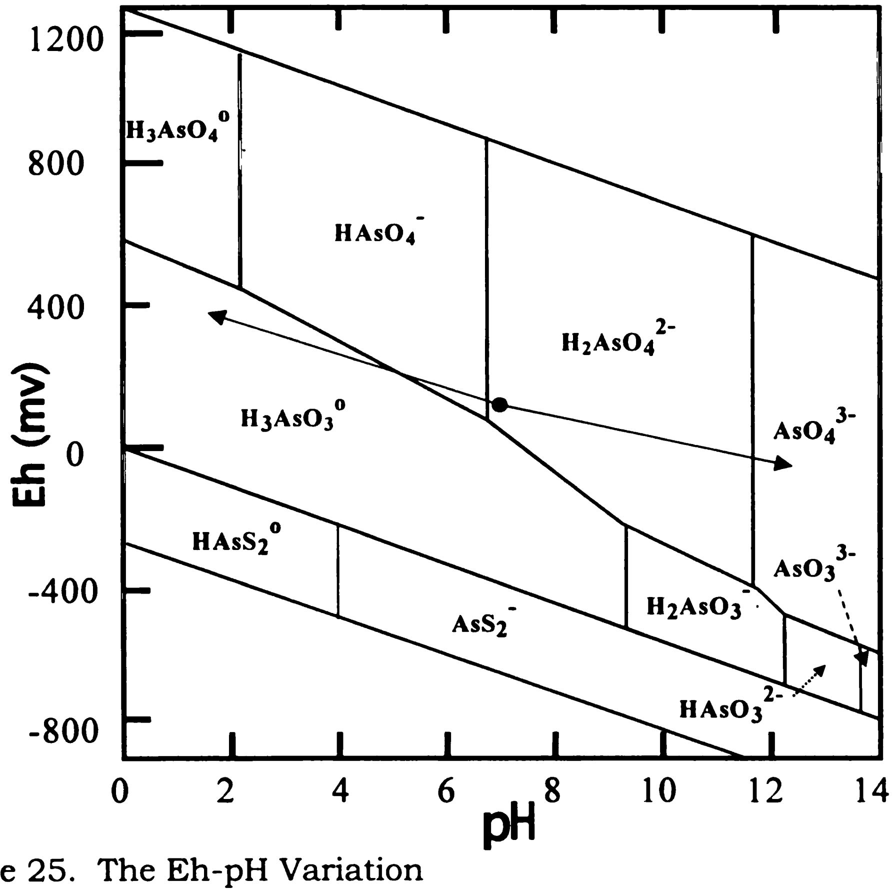

Figure 25. The Eh-pH Variation

From the Figure 24, it is observed that arsenate is removed effectively in the pH range of 5.0 to 8.5. Arsenate is not removed effectively in the pH range either below 5.0 or above 8.5. At pH above 8.5, the concentration of hydroxide ions ($OH^-$) is significantly greater than the arsenate ($HAsO_4^{2-}$) and are the predominant species in the solution. The $OH^-$ ions are competing with arsenate and prevent arsenate from attaching to the surface of the adsorbent.

The Eh-pH diagram (Figure 25) shows that the arrow crossed over the boundary between arsenate and arsenite at pH 4.0. It means that below pH 4.0 arsenate existed as arsenite. At pH 4.0 (on the boundary), the proportion of arsenate and arsenite was supposed to be 50/50, theoretically. Indeed, Figure 25 shows that 50% of arsenate was removed at pH 4.0. It means that at pH 4.0 50% of arsenic existed as arsenate and was removed. The reason why arsenate was not adsorbed at pH below 5.0 is that the predominant species changed from arsenate to arsenite below pH 4.0. The pH range of 3 to 5 is a transition range of this conversion.

## 3.4. Regeneration

Solutions of 100 ml of 100 ppb As(V) were prepared and poured into 160 ml glass bottles (bottle A and B), and then 0.05 g of plain CPG-LF were added to each bottle. The bottles were mixed using shaker at 120 rpm for 44 hour until the solution reached the equilibrium condition. Two ml samples were taken from the bottle A and B after 44 hours of shaking and the equilibrium concentration was measured. Then, 1 ml of 3 N hydrochloric acid and 1 ml of 1 N sodium hydroxide were added to bottles A and B, respectively. Bottles A and B were mixed again for 24 hours to observe the regeneration kinetics. Samples were taken after 2 hours, 6 hours and 24 hours of shaking. The followings are the results.

| | pH | ORP |
|---|---|---|
| Bottle A | 1.74 | 400 |
| Bottle B | 12.01 | 40 |

Table 10. The Condition of Solution in the Regeneration Process

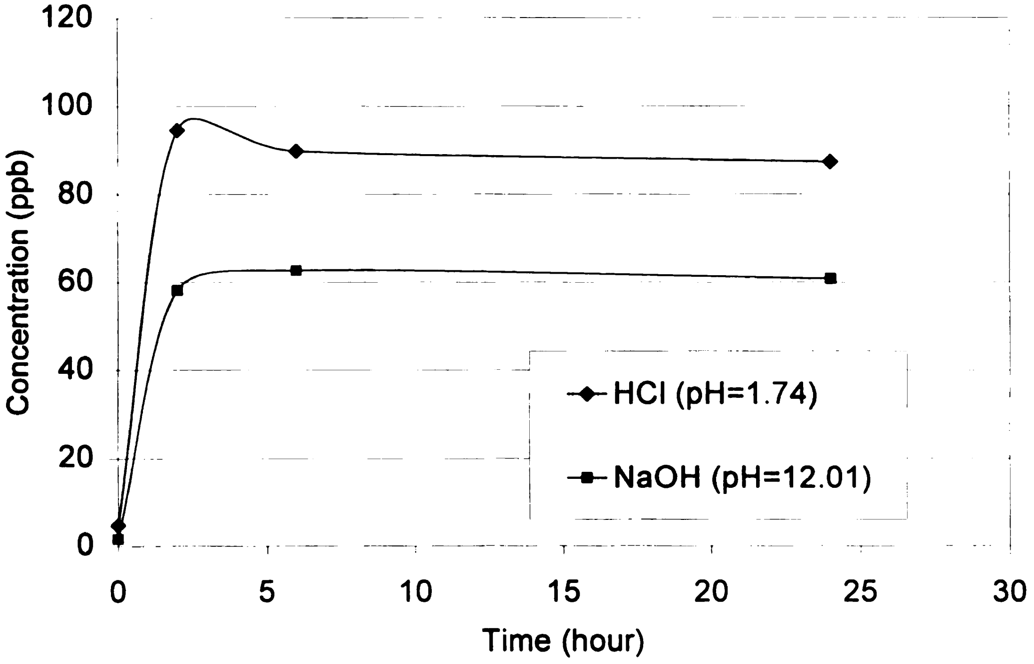

Figure 26. The Difference of Regeneration Kinetics between Acid and Base

More than 90% of arsenate was regenerated when 1 ml of 3 N HCl was added (at pH 1.74, ORP 400), whereas only 60% was regenerated when 1 ml of 1 N NaCl was added (at pH 12.01, ORP 40). Under the conditions of pH 1.74 and ORP 400, arsenic was regenerated as arsenite (neutral $H_3AsO_3$). Under the high pH condition, arsenic was regenerated as arsenate $HAsO_4^{2-}$ or $AsO_4^{3-}$. Judging from the pH effect on adsorption, it was expected that arsenite would be effectively regenerated under the high pH condition. However, it was not. Unlike the adsorption process, disorption process is not a competing process with hydroxide ions for adsorption sites, but the ion-exchange process of arsenate with hydroxide ions. It may be because the affinity of $HAsO_4^{2-}$ or $AsO_4^{3-}$ on activated carbon is high and irreversible. It is concluded that HCl is a better regenerant for arsenate regeneration.

## 3.5. Summary of Batch Test

It was observed from the batch tests that arsenate was removed very effectively by activated carbons, especially by either plain CPG-LF or plain F400. Plain DSR-C also removed arsenate effectively, but the capacity was changed when it was kept in a storage tank. Treated activated carbons also showed effective adsorption kinetics, but the adsorptive capacity seemed equal to or less than plain activated carbons. It was also observed that treated activated carbons changed the condition of the solution by releasing ferrous sulfate into solution.

The isotherm for arsenate showed that plain CPG-LF had the best adsorptive capacity (twice as much as plain F400) among activated carbons used in this experiment. There was no significant difference of adsorptive capacity between plain and treated activated carbons.

The batch tests showed that arsenite was not removed as arsenite, but removed as arsenate. Plain CPG-LF removed 90% of arsenite by oxidizing aesenite to arsenate.

Arsenate adsorption onto activate carbon was observed to be pH dependent. It was found that the optimum pH range for arsenate removal is 5.0 to 8.5.

When 1 ml of 3 N hydrochloric acid was added to solution, about 95% of the adsorbed arsenic was regenerated. However, it was observed that sodium hydroxide was not effective to regenerate arsenic.

## 4. Column Test

Column tests were conducted to observe the adsorption kinetics of arsenate and arsenite on activated carbon. In this experiment, a pump (WATSON-MARLOW 502E) was used and the flow rate was adjusted to 5.43 ml/min. A column (Flex-Column, KONTES) with the size of 1 cm diameter and 10 cm length was used. The columns were prepared by loading a certain volume of activated carbon.

## 4.1. Arsenate Adsorption through Column

10 ml of 10 ppm As(V) stock solution was taken and diluted up to 1 L to make the influent concentration of 100 ppb As(V) solution. Prepared 100 ppb As(V) solution was poured into a 5 L glass bottle. The columns were filled with 1 cm (0.785 cm$^3$) of plain CPG-LF, plain F400, plain OLC and treated OLC, respectively. The flow rate was adjusted to 5.43 cm$^3$/min and calculated contact time was 8.67 sec. Seven to ten samples were taken from the effluent during running and were measured. The following is the result of adsorption kinetics of arsenate through the column.

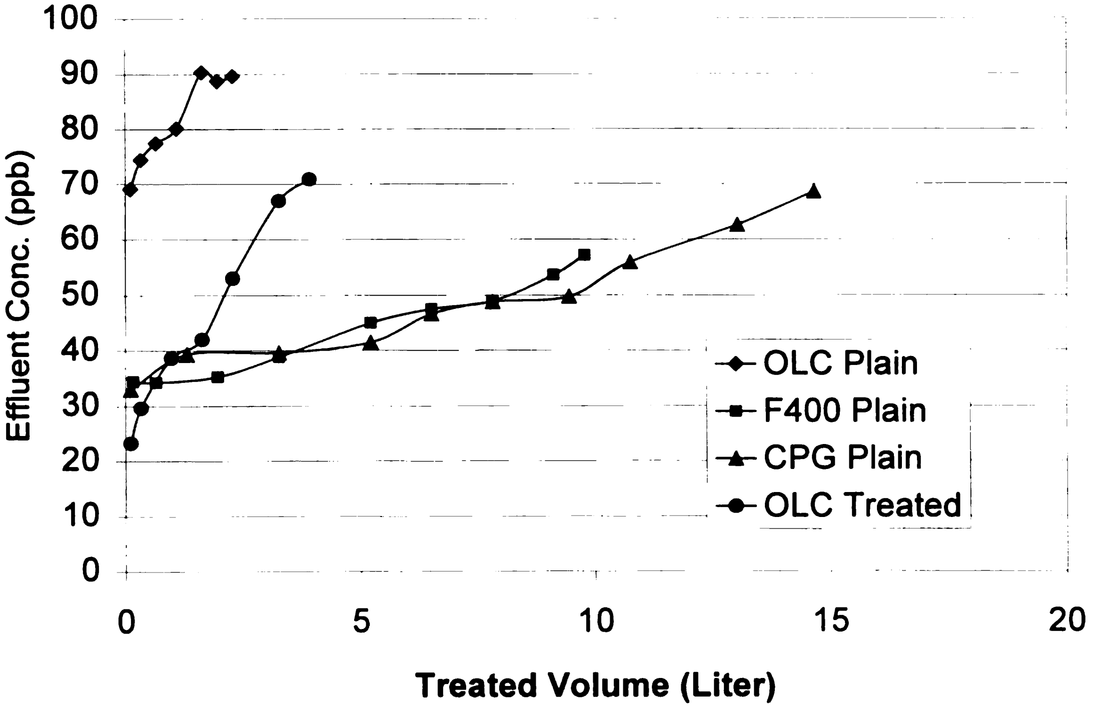

Figure 27. Adsorption Kinetics of Arsenate onto Activated Carbons Through the Column, Flow Rate=5.43 cm$^3$/min, Bed Volume=0.785 cm$^3$, Contact Time= 8.67 sec, Influent Conc.=100 ppb, pH = 7.2, ORP = 180 mV

Plain OLC did not remove arsenate effectively compared with the other activated carbons. Plain F400 and plain CPG-LF showed almost the same adsorption kinetics for arsenate removal with the initial effluent concentration of 35 ppb and the equilibrium concentration of 40 ppb. The higher equilibrium concentration compared to the batch test was due to a higher flow rate and shorter contact time. Treated OLC showed the lowest initial effluent concentration (24 ppb) among the activated carbons used in this experiment. It means that the affinity of the treated OLC to the arsenate is the strongest. However, it saturated sooner than plain F400 and plain CPG-LF because of the less adsorptive capacity. In total, plain F400 and plain CPG-LF appeared to be the best adsorbent for arsenate removal. Further study with the lower flow rate and larger bed volume is necessary to achieve longer contact time.

## 4.2. Effect of Bed Volume (Contact Time)

Two cm of plain CPG-LF (bed volume 1.57 cm$^3$) was added to the column to observe the effect of contact time on adsorption. The experiment was carried out in the same way as the previous experiment. Both the influent concentration and flow rate were maintained as before. The following is the result.

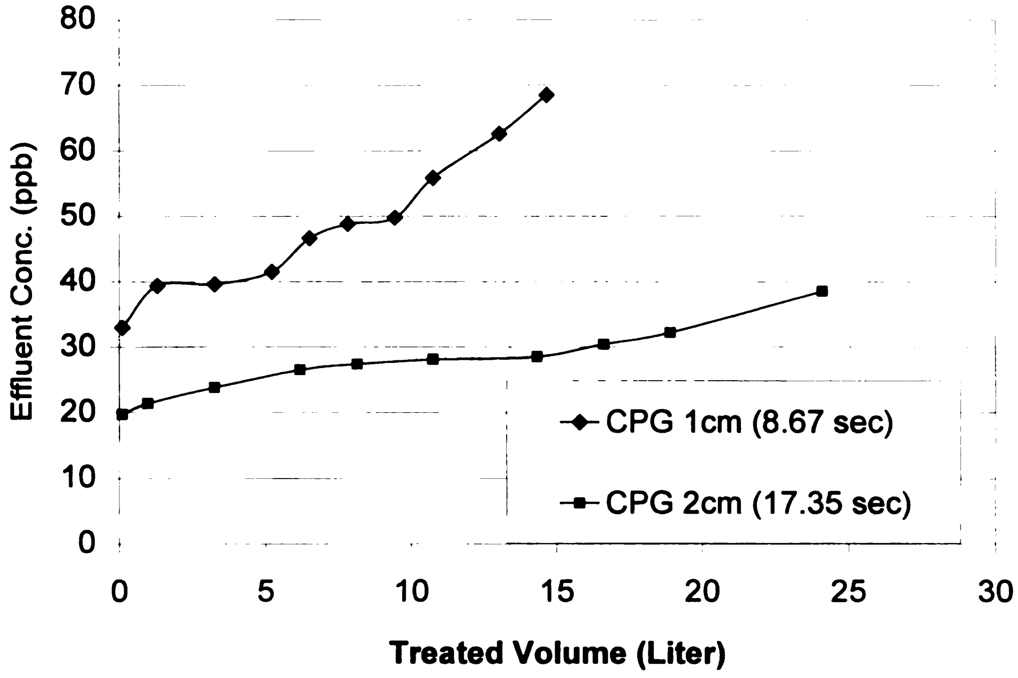

Figure 28. The Effect of Bed Volume (Contact Time) on Adsorption, Flow Rate=5.43 cm$^3$/min, Influent Conc. = 100 ppb, pH = 7.2, ORP = 180 mV

As the contact time increased, both the initial effluent concentration and the effluent equilibrium concentration decreased. A larger bed volume showed a longer running length before the break through occurred. It is assumed that if enough amount of activated carbon is loaded in the column and sufficient contact time is obtained, the equilibrium concentration would approach the same concentration as in the batch test.

## 4.3. Comparison of As(V) and As(III) Adsorption

It is necessary to maintain the arsenite in reduced form while the sample runs through the column by adding reducing agent. However, high doses of a reducing agent can effect on kinetics adsorption. So a small amount of reducing agent was used for this experiment. The pH of the solution was set near neutral condition by using reducing agent. The following is the detail method about sample preparation.

Four liter of DI water in a plastic bottle was purged with nitrogen gas for two hours. After purging, 1.0 g of sodium meta-bisulfite ($Na_2S_2O_5$) and 1.0 g of sodium sulfite ($Na_2SO_3$) were added to the purged DI water. The change of pH, DO and ORP in this process are summarized in Table 11.

| | DO (mg/L) | pH | ORP (mV) |
|---|---|---|---|
| Initial Condition of water | 2.89 | 7.22 | 185 |
| After purging with $N_2$ | 0.88 | 7.78 | 180 |
| After addition of Reducer | 0.10 | 7.02 | 60 |

Table 11. The change of DO, pH and ORP by Pre-Treatment

By this pre-treatment, the condition of pH 7.0 and ORP 60 mV were achieved, at which the predominant arsenic species is arsenate not arsenite. However, since the reaction of arsenite with oxygen is very slow and the concentration of dissolved oxygen was kept at a very low level (about 0.1 mg/L), it was assumed that arsenite was maintained in reduced form during the experiment.

The standard solution of 1000 ppm of As(III) was prepared by adding 0.17343 g of $NaAsO_2$ to 100 ml of the pretreated DI water. One ml of 1000 ppm standard solution was taken and added into 100 ml of volumetric flask to make 10 ppm standard solution. A solution of 100 ppb As(III) was prepared by taking 10 ml of 10 ppm solution and diluting it up to 1000 ml. This preparation was done under aerobic condition, so the exposure of the samples to the air was expected.

Prepared 100 ppb As(V) solution was poured into a 5 L glass bottle. The column was filled with 1 cm (0.785 $cm^3$) of plain CPG-LF. The flow rate was adjusted to 5.43 $cm^3$/min and the calculated contact time was 8.67 sec. Nine samples were taken from the effluent during running and were measured. In the middle of the experiment, the values of pH, DO and ORP were measured to determine the condition of the influent solution. The following is the result of adsorption kinetics of arsenate through the column.

| Run Length (Hour) | DO (mg/L) | pH | ORP (mV) |
|---|---|---|---|
| 0 | 0.10 | 7.02 | 60 |
| 1 | 0.10 | 6.94 | 65 |
| 2 | 0.13 | 6.86 | 70 |
| 4 | 0.14 | 6.84 | 70 |
| 6 | 0.17 | 6.65 | 75 |

Table 12. The change of DO, pH and ORP during Column Analysis.

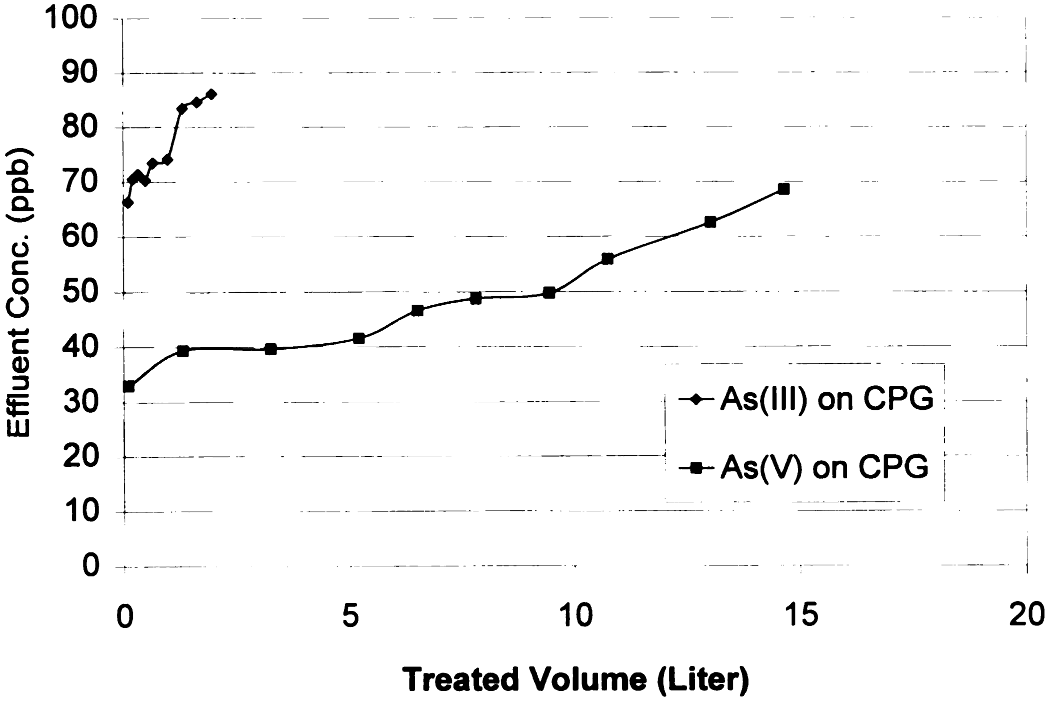

Figure 29. The Comparison of Adsorption Kinetics of As(III) with As(V)
Flow Rate=5.43 $cm^3$/min, Bed Volume=0.785 $cm^3$,
Contact Time= 8.67 sec, Influent Conc.=100 ppb,
DO= 0.10 mg/L, pH= 7.0 - 6.7, ORP= 60 - 75 mV for As(III)

Table 12 shows that the pH slightly decreases and ORP slightly increases due to the reaction of $2SO_3^{2-} + 2O_2 \Rightarrow 2SO_4^{2-}$. However, this means that oxygen was consumed by the reducing agent not by the arsenite, so arsenite should have been kept in the solution during experiment.

Figure 29 shows the adsorption kinetics of arsenate and arsenite on plain CPG-LF. Arsenite was slightly removed, but the breakthrough occurred much faster than that of arsenate.

## 4.4. Summary of Column Test

In the column tests, plain F400 and plain CPG-LF showed almost the same adsorption kinetics. Treated OLC showed stronger affinity than plain CPG-LF and plain F400 for arsenate, but it was saturated quicker because of its small adsorptive capacity. The increase of the bed volume contributed to lower the equilibrium concentration of effluent. Column analysis also showed that arsenite was not removed effectively by plain CPG-LF because of the shorter contact time than batch test.

# 5. Conclusion

All activated carbon used in this study removed arsenate effectively. The isotherm curve showed that plain CPG-LF has the best adsorptive capacity (twice as much as plain F400) for arsenate. In the column tests plain F400 and plain CPG-LF showed almost the same adsorption kinetics. Considering both adsorption kinetics and capacity, it was concluded that plain CPG-LF is the best adsorbent for arsenate. Arsenite was not effectively adsorbed on any activated carbons as arsenite at pH below 6.5. However, it was observed that plain CPG-LF oxidized arsenite to arsenate and removed the formed arsenate effectively.

The column tests showed that arsenite was not removed effectively by plain CPG-LF. This indicates that the given contact time was not enough to oxidize arsenite to arsenate. Since the contact time used in this experiment was not sufficient (about 8.7 seconds), further experimentation with longer contact times is necessary.

It was found that the removal efficiency of arsenic is dependent on the arsenate proportion of the solution. Since very high removal efficiency was achieved for arsenate with carbon adsorption under the optimal pH condition (pH 5.0-8.5), the advantage of a pre-oxidation process are apparent. Oxidants, such as chlorine and permanganate, which are available in Bangladesh, will be helpful for high removal efficiency.

The isotherm showed that 1.0 kg of plain CPG-LF can treat 20,000 L of contaminated water with influent concentration of 100 ppb until the effluent concentration is over 20 ppb. Suppose a family of six uses 40 L/day, 1kg of CPG-LF can be used for 500 days. Since the cost of CPG-LF is $3.72/kg, this system will be competitive with available techniques in Bangladesh such as Safi Filter ($4.0) and Kolshi Filter ($5.0). Moreover, an advantage of using activated carbon is that activated carbons are easily regenerated and reused by adding hydrochloric acid.

In practical use, co-occuring ions have an effect on the adsorption of arsenic on activated carbon. Laboratory tests using raw samples need to be performed.

This study suggests that activated carbon is a cost competitive point-of-use method. It is hoped that this study will provide the people in Bangladesh with the economical and easy treatment process to eliminate arsenic from their drinking water.

# Appendix

# A-1. Chemical Description

Sodium Arsenate ($Na_2HAsO_4 \cdot 7H_2O$), Sigma Chemical
S-9663, 20k2507

Sodium meta-Arsenite ($NaASO_2$), Sigma Chemical
S-7400, 79H6036

Ferrous Sulfate ($FeSO_4 \cdot 7H_2O$), Sigma Chemical
F-7002, 129H0898

Sodium Sulfite ($Na_2SO_3$), Sigma Chemical
S-8018, 121H0368

Sodium meta-Bisulfite ($Na_2S_2O_5$), Fisher
S-244, 852987

Sodium Thiosulfate ($Na_2S_2O_3$), Mallinckrodt
8096, KLJS

## A-2. Amount of Activated Carbon for Batch Test

The amount of 0.05 g, 0.1 g and 0.2 g of activated carbon were added into 100 ml of 100 ppb As(V) solution, respectively.

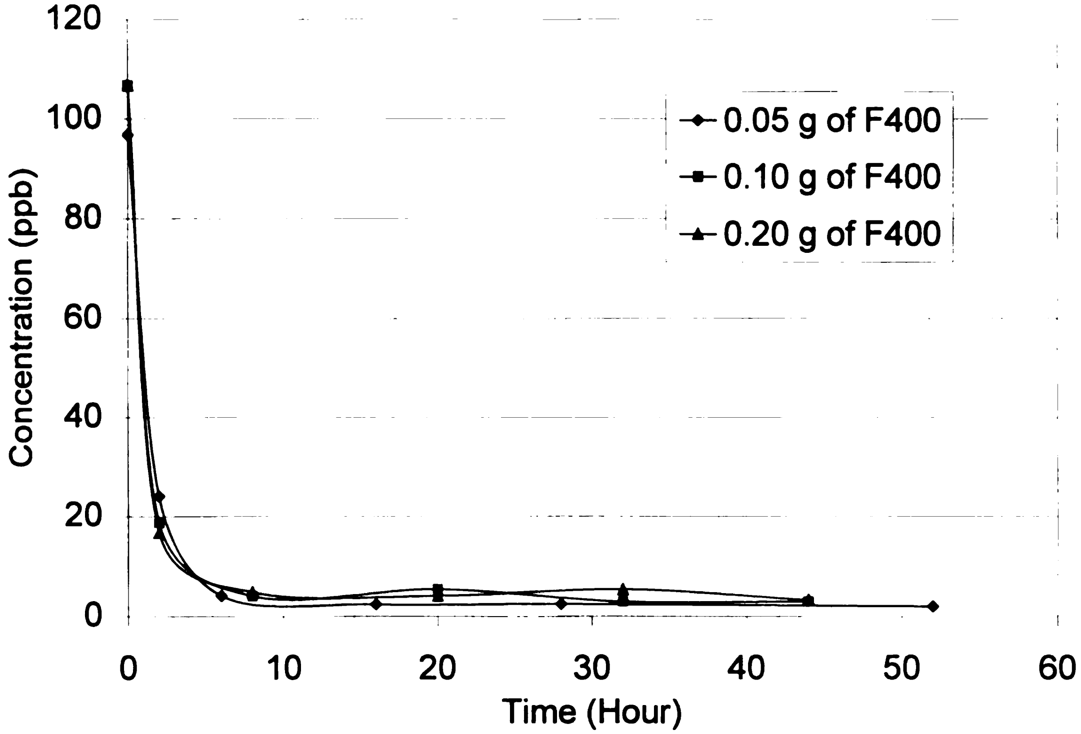

Figure 30. Optimum amount of Activated Carbon for Batch Test

There was no significant difference in adsorption kinetics among these as illustrated in Figure 30. To see the clear difference of adsorption kinetics, the minimum amount of 0.05 g of activated carbon was selected for the batch test.

## A-3. Purging Effect on DI Water

DO, pH and ORP were measured during purging DI water with nitrogen gas. The following Figure 31 is the result.

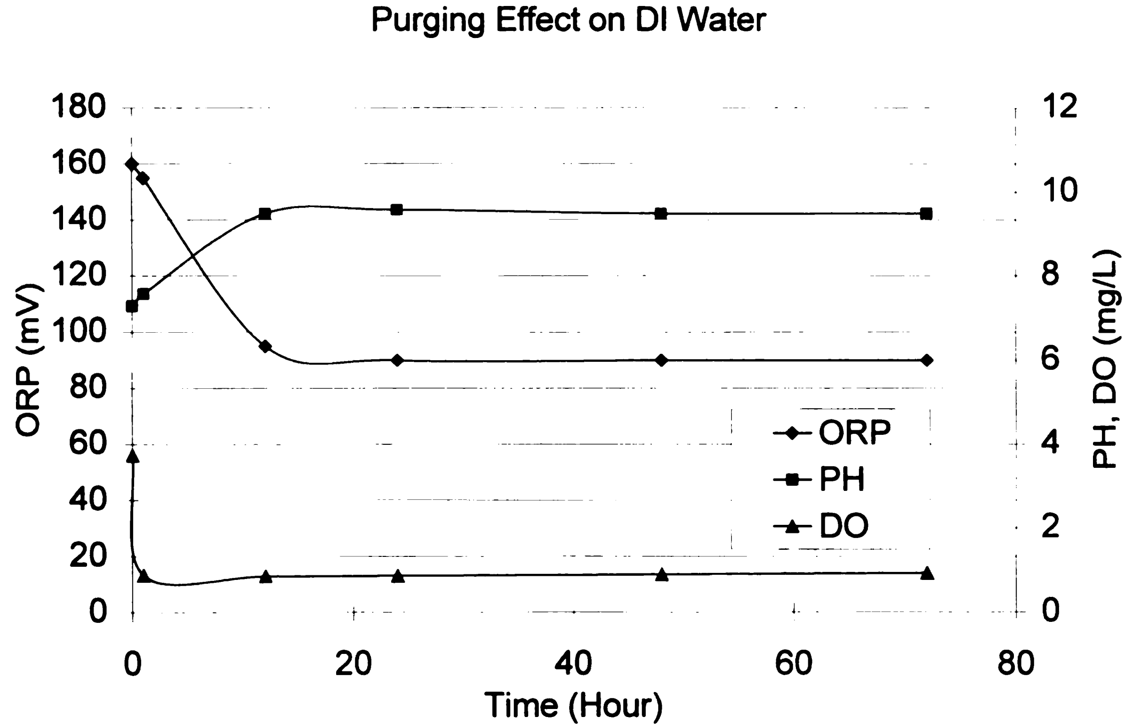

Figure 31. The Purging Effect on DO, pH and ORP

After 1 hour of purging, the concentration of dissolved oxygen decreased to 0.8 mg/L, while there was no significant change on pH and ORP. However, after 12 hours of purging, pH increased to 9.4 and ORP decreased to 90 mV.

## A-4. Shaking Effect on Sodium Thiosulfate

Five grams of sodium thiosulfate was added to 500 ml of DI water. A prepared solution of 100 ml was poured into 4 glass bottles of 160 ml capacity. Two glass bottles were shaken at 120 rpm for 3 days and the other 2 bottles were just kept for 3 days without shaking. The DO, pH and ORP were measured during the period. The following Figure 32 and Figure 33 are the results.

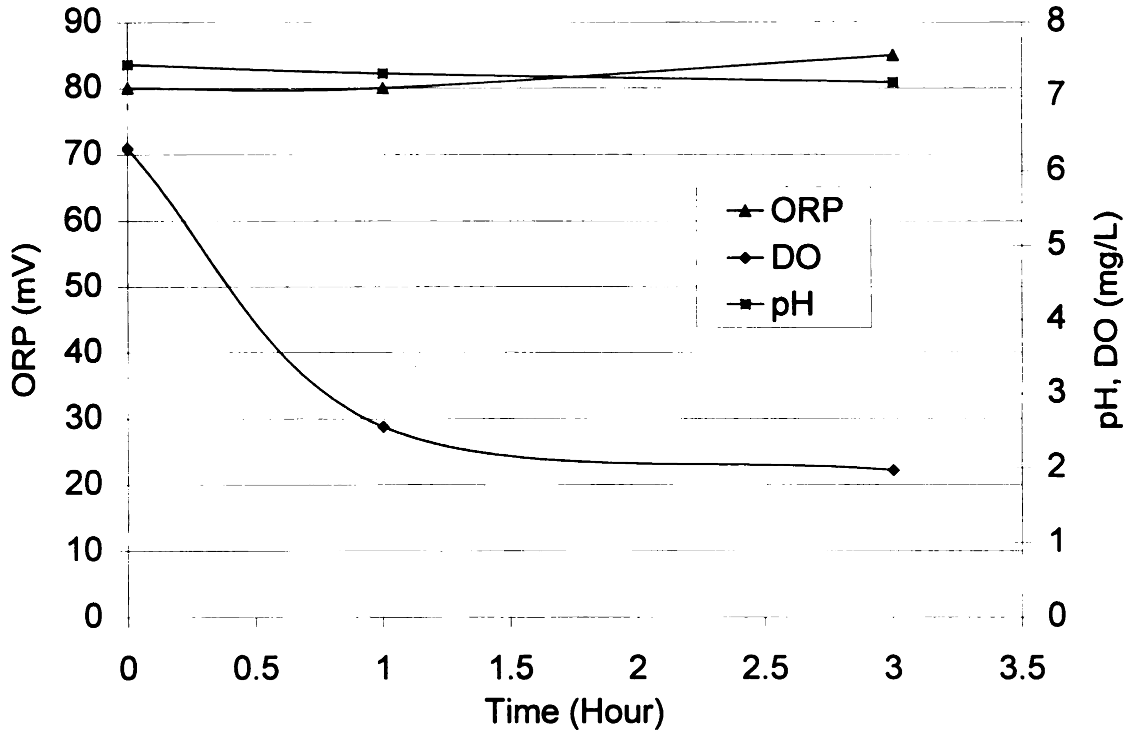

Figure 32. DO, pH and ORP Change without Shaking

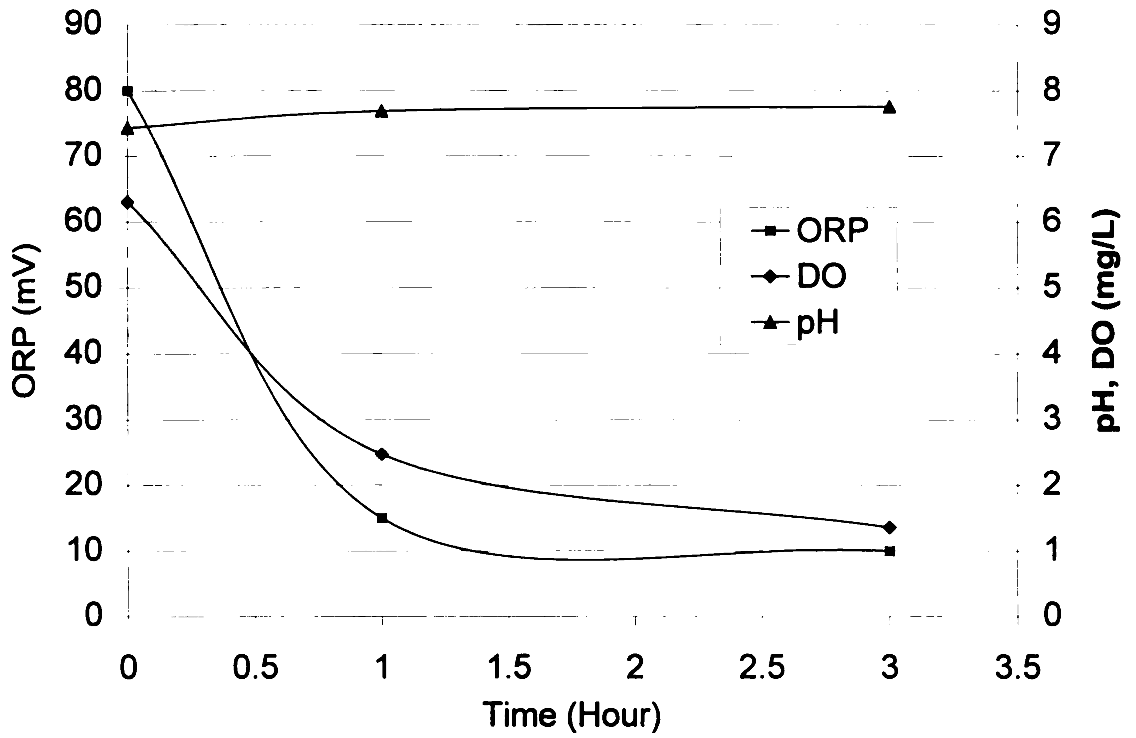

Figure 33. DO, pH and ORP Change during Shaking

Figure 32 indicates the change of the pH, DO and ORP in the solution without shaking. The pH and ORP did not change significantly.

Figure 33 shows the change of the pH, DO and ORP in the solution during shaking. The pH of the solution was raised up to 7.7 and ORP decreased down to 10 mV. Shaking accelerated the dissociation reaction $Na_2S_2O_3 \Rightarrow 2Na^+ + S_2O_3^{2-}$ so that the pH of the solution increased and ORP of the solution decreased. The produced $S_2O_3^{2-}$ reacted with oxygen and consumed the dissolved oxygen, so the concentration of DO in the solution decreased.

## A-5. Eh (Redox-Potential)

The Eh value is calculated using the following formula :

$Eh = E^o - (0.059/n) \log Q$

Example: $SO_4^{2-} + 2H^+ + 2e^- \Rightarrow SO_3^{2-} + H_2O$ $\qquad E^o = -0.04$

$Eh = E^o - (0.059/n) \log Q$

$Eh = -0.04 - (0.059/2) \log [SO_3^{2-}]/[H^+]^2[SO_4^{2-}]$

Substituting each concentration into the equation, Eh can be determined (theoritically).

## A-6. ORP Measurement

The ORP electrode measures the potential of the reaction. The ORP electrode consists of two half cells: Metallic indicating electrode and Reference electrode. The Eh value of the solution is determined by adding each signal:

$Eh = E_{metal} + E_{ref}$

An (Ag/AgCl) electrode was used for this study.

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